SUMMARY

This report on Phase II of a three phase program for "Evaluation of Methods for Hazardous Waste Analysis" provides discussions of efforts toward preparing for an interlaboratory test of the selected methods.

The efforts or results for this phase can be summarized as follows:

1. The volatile organic and semivolatile organic analysis methods were tested in Battelle's laboratory to determine if the methods were technically satisfactory and clearly defined.
2. The major modification of the method for determination of volatile compounds was the use of tetraglyme as the solvent for extraction of volatile organic compounds.
3. The major modification of the method for determination of semivolatile compounds was the use of an ultrasonic device during extraction with methylene chloride and neutralization of the matrix prior to extraction.
4. Many performance checks were incorporated into the methods to enhance quality control.
5. The interlaboratory experimental design, based on ASTM Methods E 691-69 and E 2777-77, was ultimately based on use of 9 laboratories and 8 waste samples analyzed in triplicate.
6. A Manual for Collaborators for an Interlaboratory study was prepared giving details of the method descriptions and data requirements.
7. Review of the methods and design by technical experts within Battelle, EPA, and by participants resulted in some design change.
8. Samples were prepared for the participating laboratories. The samples were spiked with 40 semivolatile and 10 volatile compounds.

TECHNICAL DISCUSSION

Overview

The objective of the Phase II effort was to develop protocols for the analysis of hazardous wastes. The intent of these methods was to identify and quantify a broad spectrum of organic compounds rather than to optimize recovery of specific constituents.

The objective was achieved through a series of simultaneous, interconnected experiments with iterations, regroupings, and reviews within Battelle and with EPA. The protocols were developed for the interlaboratory test to be evaluated during the Phase III effort. The interlaboratory test results, along with the program review inquiry results, will provide the basis for specific language and for quality control policy, events, and criteria for broadly applicable analytical protocols.

Analysis Methods

The analysis methods as described in Phase I were modified during Phase II efforts as the result of editorial reviews and application of the methods in Battelle's laboratories. Some of the modifications were necessary to remove procedural ambiguities. Other modifications involved technical change that were a result of experience or external review. The significant changes are discussed below.

Method for Determination of Volatile Organic Compounds

The changes made in the protocol for determination of volatile organic compounds since the Phase I report was written are largely the result of using tetraglyme (tetraethylene glycol dimethyl ether) rather than polyethylene glycol (PEG 400) as the solvent for extraction of volatile organic compounds.

The greatest advantage to the use of tetraglyme is that tetraglyme is a more universal solvent than PEG. In addition, tetraglyme is miscible with hydrocarbon solvents as well as with water, whereas PEG is a very poor solvent for hydrocarbons. Although PEG was found to be suitable for many of the particular waste samples included in the interlaboratory study, it would not be suitable for samples containing high levels of mineral oil or paraffin wax.

A second advantage to using tetraglyme as the extraction solvent is its lower viscosity relative to PEG. It was believed that the relatively high viscosity of PEG would make it difficult to draw up into a syringe. We found that the PEG could be handled satisfactorily by using wide-bore syringe needles; however, the large volume contained in the needle made it difficult to accurately dispense less than 20 µL. The viscosity of tetraglyme is similar to alcohol and small volumes can be dispensed using standard microsyringes. A tetraglyme extract can be introduced into the purging chamber by piercing the septum with the syringe needle. The septum is replaced after each run to avoid any carry-over of components that might have been trapped in the septum during the injection.

Tetraglyme is available from Aldrich or Eastman. We have purified tetraglyme by vacuum stripping to remove volatile components as previously recommended for the purification of PEG. The batch of tetraglyme purified initially was found to be free of interfering volatile components when analyzed by the purge and trap GC/MS procedure and was readily dispensed with a microsyringe. More recent experience with other batches of tetraglyme has indicated that additional purification is necessary. Sonification of tetraglyme solutions of representative volatile compounds, (methylene chloride, trichloroethylene, and tetrachloroethane) resulted in no significant loss of the compounds. The one-half inch probe that is described for the dispersion of samples in the method for determination of semivolatile compounds is used for sonification. The change to tetraglyme led to other changes, such as making of standard solutions, permissible use of narrow gauge syringe needles, and changes throughout the sections on extraction.

The method was written to be applicable to a broader range of solid waste types than the representative sample types chosen for this study. These changes are reflected in more general statements on means and implements for effective sample transfer, a clearer statement on obtaining and using response factors, and a more general statement on record keeping for quality control purposes. On the other hand, specificity was increased in instructions for making calibration standards, for daily performance requirements, and for estimation of major volatile compound content. Lastly, surrogate and internal standards were selected from among fluorinated (surrogate) and deuterated (internal) compounds to reduce the possibility of adding compounds for control that may occur naturally in a waste.

Method for Determination of Semivolatile Compounds

The method for determination of semivolatile compounds evolved out of efforts to improve extraction procedures and quality control. The homogenization step was changed from using a Polytron homogenizer to using an ultrasonic device. The changes in aspects of the method that relate to performance checks were all directed toward keeping the method in control so that reliable data of known quality are generated.

The solvent for extracting semivolatile compounds, methylene chloride, must be brought into contact or homogenized with the sample to be extracted. For some samples a Brinkman Polytron homogenizer is satisfactory for the extraction process. The Polytron is a mechanical shearing device that operates at sonic frequency and can homogenize most samples. However, the device is somewhat difficult to clean and the Teflon bearing deteriorates rapidly when used on a sample that has high amounts of abrasive matter such as sand or ceramic catalyst material. As discussed in the Phase I report, sonification was examined as a means for homogenization but under the conditions used was found not to be generally applicable. Nevertheless, because of the rapid wear of the Polytron (sometimes the Teflon bearing needed changing after only three or four samples) it was necessary to reexamine the use of a sonic probe to homogenize and disperse samples in solvent.

On the basis of conversations with EPA, NEIC personnel and representatives of Heat Systems, the manufacturer of the sonic probe, it appeared that the sonic probe operating conditions were not optimized in Phase I efforts. The procedure used by NEIC involved the sonification of a 1-gram sample with 10-mL of methylene chloride in a 20-mL glass scintillation vial. By using a micro probe the dispersion was reportedly to be entirely adequate. The use of a 1:10 ratio of sample to solvent instead of a 1:50 ratio probably permits a significantly better energy transfer from probe to sample. In Phase I, a larger amount of solvent was used in an attempt to minimize saturation of the solvent with the extracted components. We also included a neutralization step and a drying step to permit acids and bases to be extracted simultaneously. Nevertheless, the manufacturer reported to Battelle that by selecting the proper geometry, reducing the power output, and perhaps using a pulse mode it should be possible to achieve excellent dispersion.

Sonification studies were continued using a standard 1/2-inch probe, a 1/2-inch probe with a 5-inch half-wave extender, and an 1/8-inch microprobe. The waste samples that were studied included a wet municipal sludge, an oily soil, ethanes spent catalyst, drying bed solids, and oxychlorination catalyst pellets. An effort was made to optimize the power input, duty cycle, probe position and sample volume.

The sonification protocol that appeared to work best involved:

1. The addition of 15 mL of methylene chloride and 1 mL of buffer to 3g of sample in a 250-mL centrifuge tube.

2. Sonification for one-minute using a 1/2-inch probe with an extender and operated at a power setting of 50% and a pulsed duty cycle of 50%.

3. Addition of 135 mL of methylene chloride and sonification as above for one minute.

4. Addition of the specified amount of anhydrous sodium sulfate followed immediately by vigorous shaking.

5. A final sonification as described in 2, for one minute.

For all sonifications the probe is positioned to place the tip 0.5 to 1 cm beneath the surface of the liquid. The above protocol worked well for all samples; however, the catalyst pellets were not broken up. Although the extraction of the pellets may be complete with sonification alone, we specified that the particle size of all such samples be reduced to less than 0.1 mm diameter before the required 3-g sample is taken. A glass mortar and pestle is recommended for grinding the sample; however, many alternate methods would be suitable.

The method for the determination of semivolatile organic compounds was also revised slightly to accommodate wet sludges that do not disperse well in methylene chloride. The revision specifies the use of homogenization after the addition of sodium sulfate as well as before.

In several cases the extraction of waste samples with methylene chloride gave turbid extracts that form precipitates when concentrated. In some cases the turbidity gradually decreased upon standing. Centrifugation or filtration through a fritted funnel or through a dense glass fiber filter did not clarify the extracts. However, clarification can be achieved by filtration through a 0.2-μm membrane filter. This step was subsequently added to the procedure. This change improved the reproducibility of the residue weight determination, decreased precipitation during the concentration step, decreased the amount of nonvolatile material injected into the GC/MS system, and improved the overall reproducibility of the method.

In most cases the membrane filtration can be accomplished by using a filter holder fitted to a syringe. For extracts that are extremely difficult to filter, the filtration assembly used for the Extraction Procedure (1) works well if a fluoropolymer membrane filter and a Viton cylinder gasket are used. Only one of the samples studied required this larger assembly. Based on the above findings the method for the determination of semivolatile organic compounds in solid wastes was revised to include the use of membrane filtration.

Instructions for the use and calibration of gel permeation chromatography were added for applications of these methods beyond the scope of this study. The analyses of waste materials selected for the collaborative study do not require use of GPC cleanup.

Several procedures to enhance quality control and data quality were incorporated into the method. These include:

- Check of ion intensity ratios of decafluorotriphenylphosphine (DFTPP) in every analysis run. (This procedure was subsequently abandoned as the degradation rate of DFTPP in these waste samples was too rapid).
- Use of eight internal standards.
- Use of surrogate standards.
- Performance criterion based on response of an internal standard (D10-Phenanthrene).
- Use of column performance standards.

These procedures were incorporated in the method to provide a check of instrument performance in every analysis run. Even though performance criteria are given, the data from participating laboratories will be analyzed to determine which criteria are useful and what acceptable performance limits are useful.

Decafluorotriphenylphosphine (DFTPP) is used as the mass spectrometer tuning compound and it was considered desirable to monitor the stability and correctness of tune in every analysis run. The ions to monitor (m/e 69, 127, 275 and 442) were selected from among those used for the initial tune and on the basis of avoiding interference from ions of compounds apt to be found in extracts of wastes. However, as is discussed in the section of this report entitled Proposed Additional Studies, DFTPP solutions frequently degrade within days after a solution is exposed to air. The result is that the amount of DFTPP remaining in solution is insufficient to provide good relative ion abundance data when analyzed, therefore, we do not recommend this criterion be used in Phase III. Recommendations are made in that section for studies to eliminate the degradation problem.

The semivolatile internal standard compounds used in the program are:

D_5-bromobenzene

D_{10}-phenanthrene

D_{10}-acenaphthene

D_{12}-chrysene

D_8-naphthalene

D_{10}-biphenyl

D_{10}-pyrene

D_{12}-benzo(a)pyrene

Use of these 8 internal standards is based on the demonstrated benefit of associating an analyte compound with an internal standard compound that has a similar retention time. It was shown in the Phase I report that the repeatability of relative retention time (RRT) is highest when the RRT is near 1.0. Thus, we have selected internal standards that will give RRTs of between 0.8 and 1.2. The greater the precision of the RRT, the smaller the retention time window and the purer the mass spectra obtained. The use of internal standards having characteristic ions similar to those of the analytes produces more reproducible response factors than in cases where there are gross differences in characteristic ions.

Surrogate standards (decafluorobiphenyl, 2-fluoroaniline and pentafluorophenol) are added to the sample before extraction in order to facilitate monitoring of the extraction process. If surrogate standards are recovered poorly while other indicators are within criteria, the indication is that the extraction process is out of control (see page 233).

The method specifies that the response for D10-phenanthrene must be within set limits. This criterion forms the basis for setting the electron multiplier gain of the mass spectrometer within specified limits that provides the required dynamic range.

Column performance is assessed through use of representative acidic, basic and polar neutral compounds. These are:

D_5-aniline

D_5-nitrobenzene

D_5-phenol

D_3-2,4-dinitrophenol

The response factors of these deuterated compounds relative to D10-phenanthrene will provide information on possible deterioration of the GC column. A further check on the column is accomplished with every check standard by monitoring pentachlorophenol and 2,4-dinitro-3-chloroaniline which are present in the standards. The response factors of these compounds (relative to D10-phenanthrene) should be at least 0.05. Any degradation of the column will be immediately apparent by loss of detection of these compounds.

ASTM Review

The interlaboratory study protocol was designed to comply with ASTM Method E 691-79 (Standard Practice for Conducting An Interlaboratory Test Program to Determine the Precision of Test Methods) (2) and ASTM Method D 2777-27 (Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water) (3). The design was reviewed by Dr. Lyman Howe, Methods Advisor for ASTM D-19, Committee on Water, and Dr. Robert Paule of ASTM D-34, Committee on Wastes and ASTM E-11, Committee on Statistics. The results of those reviews initiated a change in the number of replicate analyses (from 2 to 3) and the number of samples analyzed (from 10 to 8).

The change to triplicate rather than duplicate analyses was based in part by guidelines in ASTM D2777-77. That practice contains an inequality [$r > 1 + (30/P)$] to calculate the number of replicates (r) to be made for a set of conditions. In the inequality P is the product of number of concentration levels (2), number of operators (1), number of apparatuses (1) and number of laboratories (10). Thus P for this program 2x1x1x10 or 20 $r > 1 + \frac{30}{20}$ or $r > 2.5$.

There were several strategies possible to make the test protocol satisfy the inequality. However, in order to keep the participant effort cost effective it was suggested that the number of waste samples analyzed be reduced and the number of replicates be increased to 3. That suggestion was adopted, the protocol was changed accordingly and the number of waste samples reduced to 8 samples for the determination of volatile compounds and 6 samples for the determination of semivolatile compounds.

Other comments resulting from review by ASTM can be summarized by stating that while the conditions of the test obey the principles of E 691, the program study goals require that many answers be determined from few measurements and that some assumptions must be made. The assumptions mentioned by reviewers included the following:

- Assumption of zero blank level.
- Assumption that paired spiked compounds behave identically during analysis.
- Assumption that the spike compounds do not interact with each other.
- Impossibility of obtaining a smoothed function relating precision and accuracy to concentration level.

It was not intended to determine the repeatability and reproducibility intervals for the method as a smoothed function of the level but rather for only two representative levels. It may be sufficient to determine the repeatability and reproducibility at a single level, but a second level was included simply to provide an indication of the effect of concentration.

To provide blank measurements during Phase III, the participating laboratories will analyze several process blanks but not unspiked samples. Single laboratory replicate analyses of unspiked samples have been conducted and in most cases the spike compounds were not detected in the unspiked samples. Thus, when zero is used as the blank value, it will not be an assumed value but will be based on experimental data. Admittedly, there would be greater certainty if each laboratory were to establish that the blank value is zero, but it is believed that the additional expense involved in the required measurements is not justifiable.

The assumption that the paired compounds are identical in nature is a rather critical assumption. Therefore, a pilot study was conducted as part of Phase II to provide an indication of the validity of this assumption. However, since we are not attempting to establish a smooth curve for recovery versus spike level, the assumption is not as critical as it would be otherwise. This study is discussed in a later section of this report.

We recognize that the study goals are ambitious in attempting to study both a broad range of waste types and a broad range of chemical classes. We also recognize that interactions among the spike compounds, interactions between the spike compounds and the wastes, and sample homogeneity are uncontrolled variables. The spike compounds were chosen on the basis of expected chemical stability in an effort to minimize interactions.

Waste Sample Selection

The wastes being used for the interlaboratory study are shown in Table 1. These wastes were selected:

- To represent as many waste types as possible.
- To contain a variety of compounds that are potentially hazardous.
- To represent a challenge in extraction.
- To include significant amounts of many target compounds.

This list departs somewhat from that given in the Phase I section to reduce the number of samples.

The drying-bed solids and oil refining wastes that were listed in the Phase I report were deleted because these wastes contain an oily matrix that was somewhat similar to the organic content of the contaminated soil sample. The herbicide acetone-water and TCE spent caustic samples were retained for the analysis of volatile components because they were distinctly different from

TABLE 1. WASTE SAMPLES SELECTED FOR THE INTERLABORATORY STUDY

Program Identification Number	Waste Name	Physical Description
ILS-2	Latex paint waste	Semi-solid
ILS-3	Ethanes spent catalyst	Oily powder
ILS-4	Coal-gasification tar	Tar
ILS-5	Oxychlorination spent catalyst	Pelletized solid
ILS-6	POTW sludge	Wet filter cake
ILS-7	Herbicide acetone-water	Liquid
ILS-8	Chlorinated ethanes waste	Liquid
ILS-9	Contaminated river sediment	Powder

any of the other samples in respect to volatile content. However, these two samples were not analyzed for semivolatile components because they present no extraction problems and have no unique semivolatile components.

The selected wastes were spiked and were analyzed for semivolatile and volatile compounds as shown below:

ILS-2	Semivolatile and volatile
ILS-3	Semivolatile and volatile
ILS-4	Semivolatile and volatile
ILS-5	Semivolatile and volatile
ILS-6	Semivolatile and volatile
ILS-7	Volatile only
ILS-8	Volatile only
ILS-9	Semivolatile only.

Phase III of the program included a laboratory performance evaluation. The samples for the performance evaluation include ILS-1, a methylene chloride extract of ILS-1 for semivolatile compound determinations and a tetraglyme extract of ILS-2 for volatile compound determinations. These extracts were identified as ILS-10 and ILS-11, respectively, and were included as performance evaluation samples to evaluate the reproducibility of the analysis independent of the variability of extraction. These waste samples were spiked, homogenized, and packaged in 25-ml vials with Teflon-lined screw caps. ILS-9 was the NBS Standard Reference Material No. 1645, which was already homogenized and was analyzed for reference purposes. ILS-9 provided recovery data on naturally incorporated compounds.

Use of Analysis Protocols

Target list of 200 compounds. The 60 volatile compounds and 140 semivolatile compounds on the "target list" were selected by us to provide a rigorous test of the applicability of the methods. Compounds are included on the list that were unlikely to be detected due to extraction, chromatographic or instrumental difficulties. The evaluation of the methods in Phase II has shown that some of the compounds are indeed not determined. Additional compounds will be excluded from the scope statement as a result of Phase III activities. The problem compounds identified to date should be excluded from the list for use of the method at this time. It is understood that the methods are considered to be the best available methodology and are thus currently in use within the Agency. Since the list of 200 compounds was selected to challenge the method during the course of the Collaborative Study, these compounds should not be expected to constitute a hazardous waste priority list at this time. It is suggested that the Agency applications of these methods be reviewed to determine if the method discussions are appropriate at this stage of the development and evaluation program.

Spiking

The usefulness of adding a compound (spiking) to a sample to be analyzed is a well established technique of analytical chemistry. With this technique one can obtain information on precision and recovery (accuracy) at various concentrations of the compound added. Typically, this information is obtained through replicate analysis of an unspiked sample and of the sample spiked at a minimum of 2 concentrations of the compound or compounds of interest.

A goal of this program was to test two methods, one for determination of semivolatile compounds and one for determination of volatile compounds, on a wide variety of wastes that represent all waste types. Six wastes have been selected for testing the determination of semivolatiles organic compounds and eight wastes have been selected for testing the determination of volatile organic compounds.

Because of budgetary constraints, a spiking scheme was devised that minimizes the number of analyses per test waste. The scheme involves spiking each waste in advance with 25 pairs (a total of 50 compounds) of chemically compatible reference compounds. Each of the 25 pairs represents different compound classes. The two compounds in each pair were selected on the basis of similar properties (volatility, solubility, polarity, or acidity) that would lead to the same recovery efficiencies. One compound from each pair was spiked at a relatively low level and the other at a considerably higher level. Most of the spiked compounds were different from the components in the unspiked waste. The samples were homogenized after spiking and aliquoted for shipment to the participating laboratories.

Each laboratory has been requested to analyze three replicates of each sample to determine volatile components and three replicates to determine semivolatile components. This approach was designed to provide a cost effective program. With this approach, data on the determination of unspiked components and data on the recoveries of different classes of compounds at two spike levels will be obtained simultaneously with a single run.

The high and low levels used correspond to those levels that will give approximately 250-ng and 50-ng of volatile compounds or 50-ng and 10-ng of semivolatile compounds on the GC column during analysis if 100% recovery is achieved. Since the degree of dilution or concentration required for each waste varies widely from waste-to-waste, the actual spike level used also varies widely from waste-to-waste.

A varied spiking scheme was used so that the ratio between the two compounds in each pair is not always 5:1. Six different ratios, 4:1, 5:1, 6:1, 1:4, 1:5, and 1:6, were used in a varied manner for the 25 pairs of compounds. In this way there is not any analyst-recognizable spiking pattern from waste-to-waste that can lead to a bias in the data. However, the high:low ratios are always close enough to 5:1 to avoid any significant effect on recoveries. The need for a study to ascertain that the two compounds in each pair are similar in respect to recoveries achievable at high and low concentrations was discussed in the Phase I report. That study (Pilot Study) is discussed in a later section of this report.

The spiking compounds shown in Table 2 were spiked into waste samples at the concentrations shown in Table 3 (semivolatile compounds) and Table 4 (volatile compounds).

Although the ten volatile compounds listed in Table 2 were spiked into each waste, the compound paired with 2-hexanone, namely cyclopentanone, is not purgeable under the conditions of the method, and was not determined in the interlaboratory study. The performance of cyclopentanone was not discovered in time to select and add a substitute compound.

Since the wastes were spiked at relatively high levels, it was not possible to use solutions of the spiking compounds without drastically changing the nature of the sample and interfering with the determination of volatile compounds. The only exception was in the spiking of oxychlorination catalyst pellets in which the semivolatile spike compounds were dissolved in methanol and the methanol was removed prior to spiking with volatile compounds. The volatile compounds were readily miscible with each other and were mixed to give a single solution prior to spiking. The neat semivolatile compounds were added to a glass mortar and pestle and ground to a thin slurry of finely divided particles prior to spiking.

The spiking of each waste was conducted in a manner that would yield a spiked sample that was as homogeneous as possible and not subject to phase separation. The spiking was conducted during the month of September, 1981. The procedures used for each waste are described below.

Sample ILS-1 (Contaminated Soil). Semivolatile spike compounds (4.64 g total) were measured into a mortar and ground and blended. Soil (300 g) was added to the mortar and mixing was continued to blend compounds and soil. The

TABLE 2. SPIKING COMPOUNDS

Volatile Compounds

Low-boiling Halocarbons

1,1,1-Trichloroethane
1,2-Dichloropropane

High-boiling Halocarbons

Bromoform
1,1,2,2-Tetrachloroethane

Aromatic Hydrocarbons

Ethylbenzene
Chlorobenzene

Ketones

Cyclopentanone
2-Hexanone

Nitriles

Propionitrile
2-Chloroacrylonitrile

Semivolatile Compounds

Aliphatic Halocarbons

Hexachloroethane
Hexachloropropene

Low-boiling Aromatic Halocarbons

4-Chlorotoluene
1,4-Dichlorobenzene

High-boiling Aromatic Halocarbons

Pentachlorobenzene
Hexachlorobenzene

Chlorinated Pesticides

p,p'-DDD
p,p'-DDT

Low-boiling PAHs

2-Ethylnaphthalene
1-Chloronaphthalene

Chloroanilines

4-Chloroaniline
4-Chloro-2-methylaniline

Nitroanilines

3-Nitroaniline
2-Chloro-4-nitroaniline

Pyridines

2,4,6-Trimethylpyridine
4-t-Butylpyridine

Quinolines

Quinoline
4-Methylquinoline

Haloethers

Bis(2-chloroethyl)ether
Bis(2-chloroethoxy)ethane

(continued)

TABLE 2. (Continued)

Semivolatile Compounds (continued)

Mid-boiling PAHs

Fluoranthene
Pyrene

High-boiling PAHs

1,2,5,6-Dibenzoanthracene
1,2,7,8-Dibenzocarbazole

Aromatic Nitro Cpds.

1,3-Dinitrobenzene
2,6-Dinitrotoluene

Low-acidity Phenols

2-Chlorophenol
2,6-Dimethylphenol

High-acidity Phenols

4-Nitrophenol
2,4-Dinitrophenol

Phosphates

Triphenyl phosphate
Tri-p-tolyl phosphate

Quinones

Anthraquinone
2-Methylanthraquinone

Aromatic Ketones

Acetophenone
Propiophenone

Benzoic Acids

4-Chlorobenzoic acid
4-Bromobenzoic acid

Phenoxyacetic Acids

2,4-D
2,4,5-T

mix was transferred with 100 ml of water to a glass jar and homogenized using a Polytron homogenizer for 10 minutes. The water was used to rinse the mortar and to create a slurry to promote homogenization. The contents of the jar were kept at <40°C through use of an ice bath. The homogenized slurry was transfered quantitatively to a Bramley Mill containing 595 g of the soil, the neat volatile spike compounds added, the mill sealed air tight, and the contents milled for 20 minutes. A Bramley Mill is a heavy-duty mill used for mixing rubber formulations; it consists of a stainless steel bowl, two horizontal sigmoidal blades that turn in opposite direction to provide high shear, and a gas-tight Teflon-lined cover.

Sample ILS-2 (Latex Paint Waste). A 1000 g portion of the waste and 110 g of water were homogenized with a Polytron homogenizer. A 988-g portion of this homogenized waste was added along with semivolatile spike compounds (11.9 g total) to a jar and homogenized with a Polytron for 20 minutes while keeping the temperature at <40°C with an ice bath. The volatile spiking compounds (5.8 g total) were added, the jar closed, and the contents mixed by rolling the jar for 24 hours.

TABLE 3. SEMIVOLATILE COMPOUND SPIKE LEVELS

Compound Number(1)	Compound	Spiked Pair No.(2)	Spike Concentration, μg/g ILS-1 Soil	ILS-2 Latex	ILS-3 EtCat	ILS-4 Coal Tar	ILS-5 Oxycat	ILS-6 POTW
5	4-Chlorotoluene	2	40	600	800	1,900	4	20
12	Bis(2-chloroethyl)ether	15	40	500	200	11,000	24	20
13	2-Chlorophenol	9	40	600	800	1,100	4	20
15	2,4,6-Trimethylpyridine	13	40	600	800	1,900	4	20
16	1,4-Dichlorobenzene	2	200	100	200	7,600	16	100
22	Acetophenone	18	40	100	1,000	1,900	4	20
25	Hexachloroethane	1	40	500	200	11,400	24	20
28	4-t-Butylpyridine	13	200	100	200	7,600	16	100
33	2,4-Dimethylphenol	9	200	100	200	7,600	16	100
36	Propiophenone	18	240	400	200	9,500	20	120
43	4-Chloroaniline	12	40	600	800	1,900	4	20
45	Hexachloropropene	1	160	100	1,200	1,900	4	80
50	Quinoline	14	40	500	200	11,400	24	20
51	Bis(2-chloroethoxy)ethane	15	160	100	1,200	1,900	4	80
56	4-Chloro-3-methylaniline	12	200	100	200	7,600	16	100
57	Chlorobenzoic acid	19	40	500	200	11,400	24	20
64	1-Chloronaphthalene	5	160	100	1,200	1,900	4	80
65	4-Methylquinoline	14	160	100	1,200	1,900	4	80
66	2 Ethylnaphthalene	5	40	500	200	11,400	24	20
69	4-Bromobenzoic acid	19	160	100	1,200	1,900	4	80
74	1,3-Dinitrobenzene	8	40	500	200	11,400	24	20
76	2,6-Dinitrotoluene	8	160	100	1,200	1,900	4	80
77	3-Nitroaniline	11	40	500	200	11,400	24	20
80	2,4-Dinitrophenol	10	240	400	200	9,500	20	120
84	4-Nitrophenol	10	40	100	1,000	1,900	4	20
85	Pentachlorobenzene	3	200	100	200	9,600	16	100
98	2-Chloro-4-nitroaniline	11	160	100	1,200	1,900	4	80

(continued)

TABLE 3. (Continued)

Compound Number(1)	Compound	Spiked Pair No.(2)	Spike Concentration, µg/g					
			ILS-1 Soil	ILS-2 Latex	ILS-3 EtCat	ILS-4 Coal Tar	ILS-5 Oxycat	ILS-6 POTW
100	Hexachlorobenzene	3	40	600	800	1,900	4	20
102	2,4-Dichlorophenoxyacetic acid	20	40	600	800	1,900	4	20
113	2,4,5-Trichlorophenoxyacetic acid	20	200	100	200	7,600	16	100
117	Anthraquinone	17	40	600	800	1,900	4	20
118	Fluoranthene	6	40	100	1,000	1,900	4	20
120	2-Methylanthraquinone	17	200	100	200	7,600	16	100
121	Pyrene	6	240	400	200	7,500	20	120
123	4,4'-DDD	4	40	100	1,000	1,900	4	20
125	4,4'-DDT	4	240	400	200	9,500	20	120
126	Triphenyl phosphate	16	40	600	800	1,900	4	20
132	Tri-(p-toly)phosphate	16	200	100	200	7,600	16	100
137	Dibenzocarbazole	7	160	100	1,200	1,900	4	80
139	Dibenzo(a,h)anthracene	7	40	500	200	11,400	24	20

(1) From form 2S-Study Manual
(2) From Table 2 - This report.

TABLE 4. VOLATILE COMPOUND SPIKE LEVELS

Compound Number(1)	Compound	Pair No.(2)	Spike Concentration, µg/g ILS-1 Soil	ILS-3 Latex	ILS-3 EtCat	ILS-4 Coal Tar	ILS-5 Oxycat	ILS-6 POTW	ILS-7 Herb Acet	ILS-8 Cl Et Waste
12	Propionitrile	E	5	200	500	500	25	5	600	16,000
24	2-Chloroacrylonitrile	E	25	1,000	2,000	100	5	30	100	4,000
25	1,1,1-Trichloroethane	A	20	800	500	100	5	25	100	24,000
33	1,2-Dichloropropane	A	5	200	3,000	400	20	5	500	4,000
44	Bromoform	B	25	1,000	2,000	100	5	30	100	4,000
46	2-Hexanone	D	20	800	500	100	5	25	100	24,000
47	1,1,2,2-Tetrachloroethane	B	5	200	500	500	25	5	600	16,000
50	Chlorobenzene	C	5	200	500	600	30	20	100	20,000
51	Ethylbenzene	C	30	2,500	2,500	100	5	5	400	4,000

(1) From form 2V-Study Manual
(2) From Table 2 - This report.

Sample ILS-3 (Ethanes Spent Catalyst). The semivolatile spike compounds (22.6 g total) were ground and blended in glass mortar and mixed thoroughly with 130.4 g of the waste. This mix, along with 823 g of waste and the volatile spike compounds (15 g total), was mixed in the Bramley Mill for 20 minutes.

Sample ILS-4 (Coal Tar). The semivolatile spike compounds (22.6 g total) were ground and blended in a glass mortar. Three increments of the waste sample totaling 774 g were mixed in the same mortar and transferred incrementally to a glass jar where the mix was homogenized with the Polytron at 55°C for 20 minutes. The volatile spike compounds (5.8 g total) were added and blended by rolling the jar for 12 hours. Upon standing for a few hours, a liquid layer developed comprised mainly of previously emulsified water. Fifty grams of microcrystalline cellulose was added to the mix to absorb the water and the jar was rolled for an additional 12 hours. This mix remained as a single phase.

Sample ILS-5 (Oxychlorination Catalyst). The semivolatile spike compounds (0.5 g total) were dissolved in 500 mL of methanol and the solution added to a 2-L round-bottom flask along with 1000 g of the sample. The methanol was evaporated at room temperature by placing the flask on a rotating evaporator. The sample was transferred to a wide-mouth glass jar. A cellulose extraction thimble was added to the jar, the volatile spike compounds (0.145 g total) were added to the cellulose thimble, and the jar was immediately sealed with a Teflon-lined cap and rolled for 30 hours, after which the thimble was discarded.

Sample ILS-6 (POTW). The semivolatile spike compounds (2.3 g total) were ground and blended in a glass mortar. Three 50-g aliquots of sample were added incrementally to the mortar, mixed and transferred to a glass jar along with more sample to total 997.7 g. This mix was homogenized for 10 minutes with a Polytron homogenizer. The homogenized mix was transferred to the Bramley Mill along with the volatile spike compounds and milled for 20 minutes.

Sample ILS-7 (Herbicide Acetone Waste). The volatile spike compounds (3.1 g total) were added to 997 g of filtered waste in a glass jar and the jar rolled for 4 hours.

Sample ILS-8 (Chlorinated Ethanes Waste). The volatile spike compounds (180 g total) were added to 1320 g of the waste in a glass jar and the jar rolled for 4 hours.

Sample Analyses

Determination of Volatile Organic Compounds

Analyses of waste samples spiked with volatile compounds were conducted within about five months after spiking. Results for these analyses are shown in Tables 5 through 12 in terms of amount spiked, amount found (average of triplicates), percent recovery (not corrected for background) and relative

TABLE 5. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-1 (Creosote Contaminated Soil) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g Spike	µg/g Found(1)	% Recovery	% RSD
Propionitrile	12	5	N(2)	N	ND(3)
2-Chloroacrylonitrile	24	25	1.6	6	6
1,1,1-Trichloroethane	25	20	6.3	31	9
1,2-Dichloropropane	33	5	1.9	38	5
Bromoform	44	25	10	40	17
1,1,2,2-Tetrachloroethane	47	5	3.2	63	5
Chlorobenzene	50	5	4.7	95	1
Ethylbenzene	51	30	19	62	2
2-Hexanone	46	20	7.8	31	10

(1) Average of triplicate results.
(2) Compound not detected.
(3) Not determined.

TABLE 6. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-2 (Latex Paint Waste) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g Spike	µg/g Found(1)	% Recovery	% RSD
Propionitrile	12	200	265	132	11
2-Chloroacrylonitrile	24	1,000	580	58	3
1,1,1-Trichloroethane	25	800	1,090	136	9
1,2-Dichloropropane	33	200	250	125	4
Bromoform	44	1,000	1,150	115	14
1,1,2,2-Tetrachloroethane	47	200	258	129	1
Chlorobenzene	50	200	300	150	4
Ethylbenzene	51	1,200	>1,900	>150	ND(2)
2-Hexanone	46	800	720	90	6

(1) Average of triplicate results.
(2) No meaningful value available.

TABLE 7. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-3 (Ethanes Spent Catalyst) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g Spike	µg/g Found(1)	% Recovery	% RSD
Propionitrile	12	500	N(2)	N	ND(3)
2-Chloroacrylonitrile	24	2,000	370	18	36
1,1,1-Trichloroethane	25	500	1,670	330	36
1,2-Dichloropropane	33	3,000	620	21	40
Bromoform	44	2,000	550	28	31
1,1,2,2-Tetrachloroethane	47	500	160	32	19
Chlorobenzene	50	500	183	37	8
Ethylbenzene	51	2,500	394	16	45
2-Hexanone	46	500	110	22	10

(1) Average of triplicate results.
(2) Compound not detected.
(3) Not determined.

TABLE 8. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-4 (Coal Tar) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g Spike	µg/g Found(1)	% Recovery	% RSD
Propionitrile	12	500	390	79	19
2-Chloroacrylonitrile	24	100	N(2)	N	ND(3)
1,1,1-Trichloroethane	25	100	140	140	14
1,2-Dichloropropane	33	400	480	120	11
Bromoform	44	100	87	87	16
1,1,2,2-Tetrachloroethane	47	500	N	N	ND
Chlorobenzene	50	600	690	120	9
Ethylbenzene	51	100	120	120	8
2-Hexanone	46	100	85	85	11

(1) Average of triplicate results.
(2) Compound not detected.
(3) Not determined.

TABLE 9. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-5 (Oxychlorination Catalyst) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g		% Recovery	% RSD
		Spike	Found(1)		
Propionitrile	12	25	14	56	19
2-Chloroacrylonitrile	24	5	1.2	25	20
1,1,1-Trichloroethane	25	5	0.9	18	37
1,2-Dichloropropane	33	20	1.6	8	39
Bromoform	44	5	0.7	15	44
1,1,2,2-Tetrachloroethane	47	25	11	45	20
Chlorobenzene	50	30	10	33	18
Ethylbenzene	51	5	1	20	23
2-Hexanone	46	5	2.2	43	3

(1) Average of triplicate results.

TABLE 10. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-6 (Cincinnati Dewatered Sludge) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g		% Recovery	% RSD
		Spike	Found(1)		
Propionitrile	12	5	N(2)	N	ND(3)
2-Chloroacrylonitrile	24	30	N	N	ND
1,1,1-Trichloroethane	25	25	1.2	5	5
1,2-Dichloropropane	33	5	1.3	27	40
Bromoform	44	30	N	N	ND
1,1,2,2-Tetrachloroethane	47	5	N	N	ND
Chlorobenzene	50	20	10	53	32
Ethylbenzene	51	5	3	60	39
2-Hexanone	46	25	1.6	6	72

(1) Average of triplicate results.
(2) Compound not detected.
(3) Not determined.

TABLE 11. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-7 (Herbicide Manufacturing Acetone-Water Waste) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g Spike	µg/g Found(1)	% Recovery	% RSD
Propionitrile	12	600	790	130	3
2-Chloroacrylonitrile	24	100	N(2)	N	ND(3)
1,1,1-Trichloroethane	25	100	40	40	8
1,2-Dichloropropane	33	500	330	65	4
Bromoform	44	100	43	43	7
1,1,2,2-Tetrachloroethane	47	600	200	33	9
Chlorobenzene	50	100	70	70	1
Ethylbenzene	51	400	180	45	0
2-Hexanone	46	100	87	87	3

(1) Average of triplicate results.
(2) Compound not detected.
(3) Not determined.

TABLE 12. ANALYSIS RESULTS FOR SPIKED SAMPLE ILS-8 (Chlorinated Ethanes Waste) FOR VOLATILE ORGANIC COMPOUNDS

Compound	CPD No.	µg/g Spike	µg/g Found(1)	% Recovery	% RSD
Propionitrile	12	16,000	13,700	85	8
2-Chloroacrylonitrile	24	4,000	3,900	98	3
1,1,1-Trichloroethane	25	24,000	24,700	102	2
1,2-Dichloropropane	33	4,000	3,000	75	ND(2)
Bromoform	44	4,000	2,700	68	7
1,1,2,2-Tetrachloroethane	47	16,000	14,000	88	ND
Chlorobenzene	50	20,000	17,700	88	3
Ethylbenzene	51	4,000	3,500	88	ND
2-Hexanone	46	24,000	17,700	74	3

(1) Average of triplicate results.
(2) Not determined.

standard deviation (RSD). The relative standard deviations appear consistent among spiked compounds within a particular waste sample but vary across waste types. Also, the RSDs are, in general, good when the % recovery is high.

High-level and low-level spike averages for all volatile compound spikes are shown in Table 13. These averages suggest that there is no correlation between spike level and percent recovery or RSD, but seem to suggest a relationship between sample type and analytical performance. However, there are many variables and more data will be needed before firm correlations can be made. For example, the ability to spike a sample effectively with volatile compounds is largely untested. Thus, variable recoveries among samples may relate to spiking efficiency. The ability to distribute spike compounds may be revealed by the average relative standard deviation data. For instance, as indicated in Table 13, the waste catalysts are associated with the highest RSD's.

The spike compounds with the poorest performances were propionitrile 2-chloroacrylonitrile and hexanone. The good performers in general were 1,1,1-trichloroethane, 1,2-dichloropropane, chlorobenzene and ethylbenzene. These performances tend to confirm expectations that are based on experiences with the application of Method 624 for quantifying acrylonitrile, halocarbons, and aromatic hydrocarbons in water. Highly polar compounds such as propionitrile, 2-chloroacrylonitrile, and 2-hexanone are readily solvated by water and not expected to purge well. These polar compounds may also degrade on the active surfaces of solid wastes.

TABLE 13. AVERAGE RECOVERY AND % RSD OF ALL SPIKED VOLATILE COMPOUNDS (HIGH AND LOW) IN EACH WASTE SAMPLE

	% Recovery, Average		% RSD		Spike Level Range
	High Spike	Low Spike	High Spike	Low Spike	µg/g
ILS 1	35	49	8	3	5-30
ILS 2	103	134	9	5	200-1200
ILS 3	21	34	38	21	500-3000
ILS 4	106	110	13	13	100-600
ILS 5	30	20	22	31	5-30
ILS 6	29	44	18	40	5-30
ILS 7	68	38	2	5	100-600
ILS 8	90	82	3	3	4000-24000

Determinations of Semivolatile Organic Compounds

The summary data for determinations of semivolatile compounds spiked in the waste samples are shown in Tables 14 through 20. These data include:

- Amount of a spiking compound naturally incorporated in a waste before any compounds were spiked.
- The amount of the spike.
- The amount found after spiking.
- The percent recovery.
- The relative standard deviation results from triplicate analysis of spiked samples.

The data show that the recoveries and RSDs appear to be matrix dependent not concentration-dependent. The recoveries for the most part are about 50-70% with ranges from zero to about 200%. The relative standard deviations typically range from 10% to 50%, with total range from 1% to greater than 100%. When one considers that the spiking compounds were selected to provide a severe challenge to the analysis methodology, the data appear reasonable. In fact, these data appear similar to data obtained using EPA Method 625 on similar type samples (4). For instance, previous analysis of a sample identified as Tar Column Bottoms and spiked with 10 compounds showed recoveries of from 15% to 96% and RSDs of from 15% to about 50%. Furthermore, these 10 compounds spiked in that study did not include some of the more challenging compounds included here.

Certain classes of compounds were not recovered or were poorly recovered. The compound classes that performed poorly are:

- Nitrophenols
- Carboxylic acids
- High m.w. polynuclear aromatic hydrocarbons
- Pyridines
- Anilines
- Perchlorinated hydrocarbons

In general, the poor recovery performance was correlated to poor chromatographic properties, i.e., high polarity.

The poor recoveries of perchlorinated hydrocarbons, hexachloroethane and hexachloropentene, may indicate a stability problem. The former exhibited satisfactory recovery in nearly every spiked sample, while the latter was found in only one sample.

TABLE 14. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-1 (CREOSOTE CONTAMINATED SOIL) FOR SEMIVOLATILE ORGANIC COMPOUNDS

	μg/g				
Compound	Present (1)	Spike	Found (2)	Recovery %	%RSD
4-Chlorotoluene	N	40	29	79	9
Bis(2-chloroethyl) ether	N	40	41	103	10
2-Chlorophenol	N	40	38*	94	ND
2,4,6-Trimethylpyridine	N	40	N	N	ND
1,4-Dichlorobenzene	N	200	135	68	11
Acetophenone	N	40	18	45	11
Hexachloroethane	N	40	27	68	5
4-t-Butylpyridine	N	200	148	74	23
2,4-Dimethylphenol	N	200	220	110	9
Propiophenone	N	240	120	50	8
4-Chloroaniline	N	40	N	N	ND
Hexachloropropene	N	160	N	N	ND
Quinoline	N	40	21	53	13
Bis(2-chloroethoxy) ethane	N	160	180	113	7
4-Chloro-2-methylaniline	N	200	26	13	3
4-Chlorobenzoic acid	N	40	N	N	ND
1-Chloronaphthalene	N	160	250	156	9
4-Methylquinoline	2	160	100	62	12
2-Ethylnaphthalene	N	40	36	90	5
4-Bromobenzoic acid	N	160	158*	99	ND
1,3-Dinitrobenzene	N	40	N	N	ND
2,6-Dinitrotoluene	N	160	200	125	60
3-Nitroaniline	N	40	N	N	ND
2,4-Dinitrophenol	N	240	N	N	ND
4-Nitrophenol	N	40	N	N	ND
Pentachlorobenzene	N	200	287	143	9
2-Chloro-4-nitroaniline	N	160	61**	38	24
Hexachlorobenzene	N	40	58*	145	ND
2,4-Dichlorophenoxyacetic acid	N	40	N	N	ND
2,4,5-Trichlorophenoxyacetic acid	N	200	N	N	ND
Anthraquinone	N	40	65	160	21
Fluoranthene	1,060	40	1,270	115	6
2-Methylanthraquinone	N	200	166	83	18
Pyrene	890	240	1,260	112	6
4,4'-DDD	N	40	88	220	12
4,4'-DDT	N	240	375	130	17
Triphenyl phosphate	N	N	N	N	ND
Tri-(p-tolyl) phosphate	N	200	144*	72	ND
Dibenzocarbazole	N	160	N	N	ND
Dibenzo(a,h)anthracene	92	40	N	N	ND

(1)-Result of single analysis of unspiked sample; (2)-Result of triplicate analyses of spiked sample; N-Compound not detected; *-Single result; **-Duplicate results; ND-Not determined.

TABLE 15. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-10 (EXTRACT OF CREOSOTE CONTAMINATED SOIL) FOR SEMIVOLATILE COMPOUNDS

Compound	Amount Found(1) µg/g	% Recovery	%RSD
4-Chlorotoluene	22	54	3
Bis(2-chloroethyl) ether	44	110	5
2-Chlorophenol	33	83	5
2,4,6-Trimethylpyridine	50	125	24
1,4-Dichlorobenzene	92	46	2
Acetophenone	36	90	3
Hexachloroethane	27	67	2
4-t-Butylpyridine	200	100	9
2,4-Dimethylphenol	166	83	2
Propiophenone	183	76	3
4-Chloroaniline	N(1)	N	ND
Hexachloropropene	N	N	ND
Quinoline	42	105	4
Bis(2-chloroethoxy) ethane	160	100	0
4-Chloro-2-methylaniline	76	38	15
4-Chlorobenzoic acid	N	N	ND
1-Chloronaphthalene	298	119	ND
4-Methylquinoline	119	119	ND
2-Ethylnaphthalene	61	153	6
4-Bromobenzoic acid	132	77	12
1,3-Dinitrobenzene	27	67	8
2,6-Dinitrotoluene	154	96	4
3-Nitroaniline	N	N	ND
2,4-Dinitrophenol	223	93	3
4-Nitrophenol	N	N	ND
Pentachlorobenzene	190	95	ND
2-Chloro-4-nitroaniline	142	89	*
Hexachlorobenzene	41	102	4
2,4-Dichlorophenoxyacetic acid	N	N	ND
2,4,5-Trichlorophenoxyacetic acid	N	N	ND
Anthraquinone	72	180	3
Fluoranthene	58	145	4
2-Methylanthraquinone	194	97	3
Pyrene	338	141	4
4,4'-DDD	59	147	5
4,4'-DDT	220	92	8
Triphenyl phosphate	48	120	10
Tri-(p-tolyl) phosphate	214	107	3
Dibenzocarbazole	360	227	3
Dibenzo(a,h)anthracene	63	157	13

(1) Result of triplicate analyses of one extract. Amount present in unspiked sample (see Table 14) has been subtracted from total amount found; N-Compound not detected; ND-Not determined; *-Single analytical result.

TABLE 16. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-2 (LATEX PAINT) FOR SEMIVOLATILE ORGANIC COMPOUNDS

	µg/g				
Compound	Present (1)	Spike	Found (2)	Recovery %	%RSD
4-Chlorotoluene	N	600	520	87	35
Bis(2-chloroethyl) ether	N	500	460	92	34
2-Chlorophenol	N	600	510	85	30
2,4,6-Trimethylpyridine	N	600	1,370	230	118
1,4-Dichlorobenzene	N	100	60	60	45
Acetophenone	N	100	103	103	1
Hexachloroethane	N	500	400	87	40
4-t-Butylpyridine	N	100	113*	113	ND
2,4-Dimethylphenol	N	100	106	106	52
Propiophenone	N	400	240	60	2
4-Chloroaniline	N	600	250	41	37
Hexachloropropene	N	100	N	N	ND
Quinoline	N	500	394	79	9
Bis(2-chloroethoxy) ethane	N	100	96	96	52
4-Chloro-2-methylaniline	N	100	27	27	18
4-Chlorobenzoic acid	N	500	650	130	97
1-Chloronaphthalene	N	100	143	140	31
4-Methylquinoline	N	100	111	111	33
2-Ethylnaphthalene	N	500	588	118	12
4-Bromobenzoic acid	N	100	N	N	ND
1,3-Dinitrobenzene	N	500	310	62	78
2,6-Dinitrotoluene	N	100	88	88	66
3-Nitroaniline	N	500	220	44	ND
2,4-Dinitrophenol	N	400	N	N	ND
4-Nitrophenol	N	100	N	N	ND
Pentachlorobenzene	N	100	100	100	69
2-Chloro-4-nitroaniline	N	100	N	N	ND
Hexachlorobenzene	N	600	790	130	60
2,4-Dichlorophenoxyacetic acid	N	600	N	N	ND
2,4,5-Trichlorophenoxyacetic acid	N	100	N	N	ND
Anthraquinone	N	600	490	81	5
Fluoranthene	N	100	83	83	7
2-Methylanthraquinone	N	100	80	80	ND
Pyrene	N	400	198	49	105
4,4'-DDD	N	100	296	296	47
4,4'-DDT	N	400	400	100	113
Triphenyl phosphate	N	600	400	66	62
Tri-(p-tolyl) phosphate	N	100	93	93	ND
Dibenzocarbazole	N	100	N	N	ND
Dibenzo(a,h)anthracene	N	500	N	N	ND

(1)-Results of single analysis of unspiked sample; (2)-Average result of duplicate analyses; *-Single result only; N-Compound not detected; ND-Not determined.

TABLE 17. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-3 (ETHANES SPENT CATALYST) FOR SEMIVOLATILE ORGANIC COMPOUNDS

Compound	µg/g Present (1)	Spike	Found (2)	Recovery %	%RSD
4-Chlorotoluene	N	800	808	101	21
Bis(2-chloroethyl) ether	N	200	196	98	14
2-Chlorophenol	N	800	526	66	16
2,4,6-Trimethylpyridine	N	800	N	N	ND
1,4-Dichlorobenzene	N	200	138	67	23
Acetophenone	N	1,000	755	76	16
Hexachloroethane	N	200	138	69	34
4-t-Butylpyridine	N	200	90	45	9
2,4-Dimethylphenol	N	200	N	N	ND
Propiophenone	N	200	108	54	19
4-Chloroaniline	N	800	N	N	ND
Hexachloropropene	N	1,200	77**	6	4
Quinoline	N	200	128	64	9
Bis(2-chloroethoxy) ethane	N	1,200	1,330	111	26
4-Chloro-2-methylaniline	N	200	N	N	ND
4-Chlorobenzoic acid	N	200	N	N	ND
1-Chloronaphthalene	N	1,200	N	N	ND
4-Methylquinoline	N	1,200	1,740	145	43
2-Ethylnaphthalene	N	200	173	86	60
4-Bromobenzoic acid	N	1,200	560	47	64
1,3-Dinitrobenzene	N	200	N	N	ND
2,6-Dinitrotoluene	N	1,200	1,160	97	21
3-Nitroaniline	N	200	N	N	ND
2,4-Dinitrophenol	N	200	N	N	ND
4-Nitrophenol	N	1,000	N	N	ND
Pentachlorobenzene	200	192	96	44	
2-Chloro-4-nitroaniline	N	1,200	135**	11	1
Hexachlorobenzene	N	800	896	112	4
2,4-Dichlorophenoxyacetic acid	N	800	N	N	ND
2,4,5-Trichlorophenoxyacetic acid	N	200	N	N	ND
Anthraquinone	N	800	750	94	22
Fluoranthene	N	1,000	940	94	23
2-Methylanthraquinone	N	200	184*	92	ND
Pyrene	N	200	38*	19	ND
4,4'-DDD	N	1,000	1,270	127	31
4,4'-DDT	N	200	N	N	ND
Triphenyl phosphate	N	800	738	92	14
Tri-(p-tolyl) phosphate	N	200	143*	71	ND
Dibenzocarbazole	N	1,200	N	N	ND
Dibenzo(a,h)anthracene	N	200	N	N	ND

(1)-Result of single analysis of unspiked sample; (2)-Average result of triplicate analyses; N-Compound not detected; *-Single result; **-Duplicate results; ND-Not determined.

TABLE 18. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-4 (COAL TAR) FOR SEMIVOLATILE ORGANIC COMPOUNDS

Compound	µg/g Present (1)	µg/g Spike	µg/g Found (2)	Recovery %	%RSD
4-Chlorotoluene	N	1,900	1,810	95	49
Bis(2-chloroethyl) ether	N	11,400	12,410	109	34
2-Chlorophenol	N	1,900	2,800*	147	*
2,4,6-Trimethylpyridine	N	1,900	N	N	ND
1,4-Dichlorobenzene	N	7,600	6,900	90	35
Acetophenone	N	1,900	1,300	68	14
Hexachloroethane	N	11,400	10,800	95	38
4-t-Butylpyridine	N	7,600	7,500	99	31
2,4-Dimethylphenol	900	7,600	9,170	108	44
Propiophenone	N	9,500	6,400	67	9
4-Chloroaniline	N	1,900	1,060*	56	*
Hexachloropropene	N	1,900	N	N	ND
Quinoline	N	11,400	2,100	18	11
Bis(2-chloroethoxy) ethane	N	1,900	1,500	81	62
4-Chloro-2-methylaniline	N	7,600	N	N	ND
4-Chlorobenzoic acid	N	11,400	11,930**	105	128
1-Chloronaphthalene	N	1,900	2,700	140	27
4-Methylquinoline	N	1,900	2,900	150	29
2-Ethylnaphthalene	N	11,400	1,600	14	10
4-Bromobenzoic acid	N	1,900	N	N	ND
1,3-Dinitrobenzene	N	11,400	8,600	75	58
2,6-Dinitrotoluene	N	1,900	2,100**	108	56
3-Nitroaniline	N	11,400	N	N	ND
2,4-Dinitrophenol	N	9,500	8,200**	86	48
4-Nitrophenol	N	1,900	N	N	ND
Pentachlorobenzene	N	7,600	8,300	109	50
2-Chloro-4-nitroaniline	N	1,900	N	N	ND
Hexachlorobenzene	N	1,900	900*	48	*
2,4-Dichlorophenoxyacetic acid	N	1,900	N	N	ND
2,4,5-Trichlorophenoxyacetic acid	N	7,600	N	N	ND
Anthraquinone	N	1,900	1,200**	65	34
Fluoranthene	4,600	1,900	15,600	240	7
2-Methylanthraquinone	N	7,600	6,600	86	8
Pyrene	19,000	9,500	19,800	70	7
4,4'-DDD	N	1,900	2,500	130	60
4,4'-DDT	N	9,500	8,600	91	79
Triphenyl phosphate	N	1,900	1,200**	63	45
Tri-(p-tolyl) phosphate	N	7,600	6,360**	84	12
Dibenzocarbazole	N	1,900	N	N	ND
Dibenzo(a,h)anthracene	5,000	11,400	N	N	ND

(1)-Result of single analysis of unspiked sample; (2)-Average result of triplicate analyses; N-Compound not detected; *-Single result; **-Duplicate results; ND-Not determined.

TABLE 19. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-5 (OXYCHLORINATED SPENT CATALYST) FOR SEMIVOLATILE ORGANIC COMPOUNDS

	μg/g				
Compound	Present (1)	Spike	Found (2)	Recovery %	%RSD
4-Chlorotoluene	N	4	0.17*	4	ND
Bis(2-chloroethyl) ether	N	24	8.6**	36	2
2-Chlorophenol	N	4	N	N	ND
2,4,6-Trimethylpyridine	N	4	4.3*	108	ND
1,4-Dichlorobenzene	0.7	16	1.3**	8	11
Acetophenone	N	4	0.9**	23	12
Hexachloroethane	N	24	1.6**	7	12
4-t-Butylpyridine	N	16	2.8*	18	ND
2,4-Dimethylphenol	N	16	N	N	ND
Propiophenone	N	20	5**	26	9
4-Chloroaniline	N	4	N	N	ND
Hexachloropropene	N	4	N	N	ND
Quinoline	N	24	2.7**	9	120
Bis(2-chloroethoxy) ethane	N	4	2.7**	67	6
4-Chloro-2-methylaniline	N	16	N	N	ND
4-Chlorobenzoic acid	N	24	8*	34	ND
1-Chloronaphthalene	N	4	2.4**	60	7
4-Methylquinoline	N	4	0.6*	15	ND
2-Ethylnaphthalene	N	24	11**	46	6
4-Bromobenzoic acid	N	4	N	N	ND
1,3-Dinitrobenzene	N	24	18**	76	0.8
2,6-Dinitrotoluene	N	4	3.4**	86	9
3-Nitroaniline	N	24	N	N	ND
2,4-Dinitrophenol	N	20	16**	81	15
4-Nitrophenol	N	4	N	N	ND
Pentachlorobenzene	N	16	13**	80	6
2-Chloro-4-nitroaniline	N	4	0.7*	17	ND
Hexachlorobenzene	N	4	3	77	1.5
2,4-Dichlorophenoxyacetic acid	N	4	N	N	ND
2,4,5-Trichlorophenoxyacetic acid	N	16	N	N	ND
Anthraquinone	N	4	1	26	9
Fluoranthene	N	4	1	29	13
2-Methylanthraquinone	N	16	5**	30	4
Pyrene	N	20	6**	28	2
4,4'-DDD	N	4	5	116	30
4,4'-DDT	N	20	28	139	20
Triphenyl phosphate	N	4	2	46	24
Tri-(p-tolyl) phosphate	N	16	8	49	5
Dibenzocarbazole	N	4	N	N	ND
Dibenzo(a,h)anthracene	N	24	N	N	ND

(1)-Result of single analysis of unspiked sample; (2)-Average result of triplicate analyses; N-Compound not detected; *-Single result; **-Duplicate results; ND-Not determined.

TABLE 20. SUMMARY OF ANALYSIS DATA FOR SPIKED SAMPLE ILS-6 (CINCINNATI DEWATERED SLUDGE) FOR SEMIVOLATILE ORGANIC COMPOUNDS

Compound	µg/g Present (1)	 Spike	 Found (2)	Recovery %	%RSD
4-Chlorotoluene	N	20	10	47	50
Bis(2-chloroethyl) ether	N	20	16	78	28
2-Chlorophenol	N	20	14**	73	45
2,4,6-Trimethylpyridine	N	20	N	N	N
1,4-Dichlorobenzene	N	100	46	46	39
Acetophenone	N	20	8	42	7
Hexachloroethane	N	20	N	N	N
4-t-Butylpyridine	N	100	84	84	42
2,4-Dimethylphenol	N	100	88	88	52
Propiophenone	N	120	45	38	6
4-Chloroaniline	N	20	N	N	N
Hexachloropropene	N	80	N	N	N
Quinoline	N	20	10	50	8
Bis(2-chloroethoxy) ethane	N	80	60	74	42
4-Chloro-2-methylaniline	N	100	24	24	27
4-Chlorobenzoic acid	N	20	N	N	N
1-Chloronaphthalene	N	80	92	116	33
4-Methylquinoline	N	80	80	100	37
2-Ethylnaphthalene	N	20	21	108	13
4-Bromobenzoic acid	N	80	N	N	N
1,3-Dinitrobenzene	N	20	N	N	N
2,6-Dinitrotoluene	N	80	N	N	N
3-Nitroaniline	N	20	N	N	N
2,4-Dinitrophenol	N	120	N	N	N
4-Nitrophenol	N	20	N	N	N
Pentachlorobenzene	N	100	96	96	62
2-Chloro-4-nitroaniline	N	80	N	N	N
Hexachlorobenzene	N	20	38*	193	N
2,4-Dichlorophenoxyacetic acid	N	20	N	N	N
2,4,5-Trichlorophenoxyacetic acid	N	100	N	N	N
Anthraquinone	N	20	9	48	23
Fluoranthene	N	20	19	78	21
2-Methylanthraquinone	4	100	70	70	10
Pyrene	N	120	103	83	10
4,4'-DDD	4	20	58	290	63
4,4'-DDT	N	120	N	N	N
Triphenyl phosphate	N	20	14*	70	N
Tri-(p-tolyl) phosphate	N	100	90*	90	N
Dibenzocarbazole	N	80	48*	60	N
Dibenzo(a,h)anthracene	N	20	N	N	N

(1)-Result of single analysis of unspiked sample; (2)-Average result of triplicate analyses; N-Compound not detected; *-Single result; **-Duplicate results; ND-Not determined.

The above data were obtained early in the program and later were checked by analysis in our laboratory of Performance Evaluation Sample ILS-10, which is an extract of sample ILS-1. The analysis results of ILS-10 are shown in Table 15 immediately following the ILS-1 data. The results of analysis of sample ILS-10 support the conclusion that nitro phenols, carboxylic acids, hexachloropropene and anilines perform poorly.

Several compounds specifically 2,4,6-trimethylpyridine, 1,3-dinitrobenzene, triphenyl phosphate, dibenzocarbozole, and dibenzo(a,h)anthracene, that were not found initially in ILS-1 were found in ILS-10. The improved detection may have resulted from better GC/MS performance as well as from a better extraction technique (use of ultrasonic energy).

Not only are the recoveries better for many of the compounds in ILS-10 than for ILS-1 but also the relative standard deviations appear to be better. It may be premature to make that judgment, in as much as the analysis of ILS-1 was done on extractions of three separate sample aliquots, whereas the analysis of ILS-10 represented replicate analyses of an extract of one sample aliquot. Thus the RSD for the ILS-10 data includes only analysis variation and omits extraction variations.

Pilot Study

The spiking scheme used for this program is unique. The scheme involves spiking each waste with a series of compound pairs. Compounds in each pair were chosen to be chemically similar and it was assumed that analytical performance is similar. One compound of each pair was spiked at a high concentration and the other at a low concentration. The benefit of such an arrangement is that one sample so spiked will, in a single analysis, provide precision and recovery (accuracy) information at two different concentrations. This would lead to a considerable saving in analyses costs.

Because the scheme is a departure from standard ways of obtaining information on precision and recovery as a function of concentration, it seemed prudent to investigate the effectiveness of such a design in a small single laboratory study before using it in the interlaboratory study. The objective of this pilot study was to determine whether spiked compound pairs will have similar analytical recoveries at both high and low concentrations.

The pilot study was conducted on 2 waste samples, latex paint waste and POTW sludge. The design of the study included triplicate analyses of unspiked wastes, triplicate analyses of the wastes with one of each compound pair (see Table 2) spiked at a high concentration and the other spiked at one fifth that level, and triplicate analyses of the wastes with the compound pair concentration reversed. The latex paint waste was spiked at 1250 µg/g and 250 µg/g and the POTW sludge was spiked at 250 µg/g and 50 µg/g.

The results obtained from this study are shown in Tables 21 and 22. In most cases, with the exception of the benzoic acids, phenoxyacetic acids,

TABLE 21. RECOVERY OF SPIKED COMPOUNDS FROM POTW SLUDGE

Compound	% Recovery at 50 µg/g		% Recovery at 250 µg/g	
	Mean[a]	SD	Mean[a]	SD
Hexachloroethane	70	11	54	8
Hexachloropropane	50	6	50	2
4-Chlorotoluene	60	4	54	6
1,4-Dichlorobenzene	57	5	51	5
Pentachlorobenzene	74	7	60	5
Hexachlorobenzene	64	2	60	6
4,4'-DDD	79	12	66	6
4,4'-DDT	57	8	56	4
2-Ethylnaphthalene	69	11	63	3
1-Chloronaphthalene	63	5	57	4
Fluoranthene	72	6	63	2
Pyrene	70	3	62	6
1,3-Dinitrobenzene	49	8	56	2
2,6-Dinitrotoluene	75	16	59	5
2-Chlorophenol	63	9	55	3
2,4-Dimethylphenol	77	4	64	5
4-Nitrophenol	42	5	60	4
2,4-Dinitrophenol	41	3	48	4
4-Chloroaniline	55	8	46	4
4-Chloro-2-methylaniline	66	3	55	5
3-Nitroaniline	50	1	61	4
2-Chloro-4-nitroaniline	41	12	65	5
2,4,6-Trimethylpyridine	108	7	116	4
4-t-Butylpyridine	62	1	56	5
Quinoline	56	5	53	3
4-Methylquinoline	62	3	58	3
Bis(2-chloroethyl)ether	78	3	63	7
Bis(2-chloroethoxy)ethane	53	5	55	3
Triphenyl phosphate	77	5	65	2
Tri-p-tolyl phosphate	78	3	70	7
Anthraquinone	78	12	64	4
2-Methylanthraquinone	86	6	66	7
Acetophenone	61	5	56	7
Propiophenone	59	4	56	3
4-Chlorobenzoic acid	59	9	55	5
4-Bromobenzoic acid	ND[b]	ND	56	7
2,4-D	ND	ND	ND	ND
2,4,5-T	ND	ND	ND	ND

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[a] Average of 3 replicates.
[b] ND = compound not detected.

TABLE 22. RECOVERY OF SPIKED COMPOUNDS FROM LATEX PAINT WASTE

Compound	% Recovery at 250 μg/g		% Recovery at 1250 μg/g	
	Mean(a)	SD	Mean(a)	SD
Hexachloroethane	71	5	84	5
Hexachloropropene	51	4	95	2
4-Chlorotoluene	72	2	81	8
1,4-Dichlorobenzene	74	7	83	3
Pentachlorobenzene	69	1	91	3
Hexachlorobenzene	64	4	94	3
4,4'-DDD	73	3	80	6
4,4'-DDT	54	5	96	1
2-Ethylnaphthalene	85	1	89	2
1-Chloronaphthalene	94	8	94	3
Fluoranthene	84	1	89	5
Pyrene	89	5	92	1
1,3-Dinitrobenzene	16	11	84	9
2,6-Dinitrotoluene	82	6	102	8
2-Chlorophenol	72	1	86	5
2,4-Dimethylphenol	76	9	97	1
4-Nitrophenol	44	19	80	12
2,4-Dinitrophenol	ND(b)	ND	113	27
4-Chloroaniline	75	10	94	6
4-Chloro-2-methylaniline	84	4	99	4
3-Nitroaniline	15	3	69	7
2-Chloro-4-nitroaniline	ND	ND	107	4
2,4,6-Trimethylpyridine	57	4	64	5
4-t-Butylpyridine	78	5	88	1
Quinoline	89	5	91	8
4-Methylquinoline	82	3	104	4
Bis(2-chloroethyl)ether	83	2	86	4
Bis(2-chloroethoxy)ethane	64	8	101	2
Triphenyl phosphate	54	8	89	3
Tri-p-tolyl phosphate	49	10	97	5
Anthraquinone	64	2	90	7
2-Methylanthraquinone	47	3	93	2
Acetophenone	96	2	94	4
Propiophenone	90	6	94	2
4-Chlorobenzoic acid	ND	ND	85	42
4-Bromobenzoic acid	ND	ND	ND	ND
2,4-D	ND	ND	ND	ND
2,4,5-T	ND	ND	ND	ND

(a) Average of 3 replicates.
(b) ND = compound not detected.

pyridines, and some of the nitro compounds, the two compounds in each set give similar recoveries at both levels within the precision of the method. Underivatized benzoic and phenoxyacetic acids were expected to have poor chromatographic properties, even on good fused silica capillary columns. These compounds were included to challenge the method and thereby to establish method limitations. The pyridines and nitro compounds and especially the nitrophenols have poor chromatographic properties and for these compounds it will be difficult to separate analytical and extraction variables.

Response Factor Study

The quality assurance protocol for this collaborative study included a QC Protocol for Fused Silica Capillary Columns that was developed by Acurex under the direction of Mr. Drew Sauter, EPA-LV and modified by Battelle for this study. The protocol included specific instructions for calculating response factors and criteria for acceptance.

In order that response factor criteria given in the QA protocol for collaborators might be realistic in absolute value and acceptable variation, the response factors for the semivolatile compounds in the calibration standard were determined in three different laboratories: Battelle, EMSL-LV, and Raltech. A three laboratory study was considered minimum to provide reasonable certainty on an average response factor and a standard deviation from which QA limits could be set.

Because the limits established will need to be met by participants in the interlaboratory study, compounds that may present chromatography problems or compounds having quantification ions with masses that differ too much from the mass of the internal standard quantification ion were not included in an initial review of the RF study data.

By using an initial mass difference criterion of ±20 atomic mass units 43 of the 140 compounds in the calibration standards were acceptable as compounds for which to set RF limits. These 43 compounds were evaluated on the basis of the RF RSD from the three laboratory study. As a result of this study 11 compounds were eliminated from further consideration as compounds for RF limit criteria.

Further examination showed reasonably good agreement for response factors for several compounds that have quantification ions with masses that differ by more than 20 a.m.u. from mass of the internal standard quantification ion. We therefore, reconsidered the ±20 a.m.u. range that was previously selected as an acceptable range and selected 18 additional compounds to be subject to specified RF limits. The additional compounds include primarily anilines and phenols. The total list of 50 compounds with response factor data, recommended specified response factors, and a.m.u. difference between the quantification ion and the internal standard quantification ion is given in Table 23.

We recommended that the participants in the interlaboratory study be required to meet the specified response factors for all 50 compounds in all calibration runs at the 50 μg/ml level within a precision of ±40%. For many

TABLE 23. RECOMMENDED COMPOUND RESPONSE FACTORS TO BE MONITORED DURING THE INTERLABORATORY COMPARISON STUDY

No.	Compound	Recommended RF	RF from Given Source(a) A	B	C	%RSD of RF From Source B	a.m.u. Difference (b)
1	Bromobenzene	1.00	-	1.04	0.94-1.18	12	5
2	Bis(2-chloroethyl) ether	1.10	-	1.13	1.08-1.36	17	11
3	Benzyl chloride	1.90	-	1.89	1.59-2.03	16	9
4	1,2-Dichlorobenzene	0.30	-	0.31	0.29-0.39	12	10
5	N-Methylaniline	0.65	-	0.57	0.49-0.70	16	20
6	4-Methylaniline	0.65	-	0.51	0.64-0.88	37	29
7	Hexachloroethane	0.16	-	0.15	0.12-0.21	16	19
8	N,N,-Dimethylaniline	0.60	-	0.58	0.50-0.65	18	16
9	1,2,4,5-Tetramethylbenzene	0.70	-	0.72	0.69-0.85	13	17
10	2-Nitrophenol	0.18	0.22	0.19	0.15-0.28	30	3
11	2,4-Dimethylphenol	0.34	0.32	0.34	0.26-0.45	13	14
12	2,6-Dimethylaniline	0.40	-	0.42	0.33-0.49	10	15
13	2,6-Dichlorophenol	0.30	-	0.29	0.21-0.31	17	26
14	1,2,4-Trichlorobenzene	0.32	0.32	0.32	0.26-0.40	14	44
15	Naphthalene	1.00	1.08	0.99	1.05-1.42	7	8
16	4-Chloroaniline	0.40	-	0.45	0.29-0.51	11	9
17	2,4-Dichlorophenol	0.30	0.30	0.30	0.22-0.33	19	26
18	Hexachlorobutadiene	0.14	0.13	0.16	0.10-0.17	19	89
19	Quinoline	0.70	-	0.73	0.15-0.95	11	7
20	3,4-Dichloroaniline	0.50	-	0.54	0.37-0.65	17	3
21	2-Chloro-4-nitrophenol	0.15	-	0.15	0.10-0.20	36	9
22	2,3-Dimethylnaphthalene	1.00	-	0.95	1.01-1.11	11	8
23	Dimethyl phthalate	1.30	-	1.29	0.87-1.52	9	1
24	Acenaphthene	1.00	-	0.95	0.08-1.12	11	10
25	2,4-Di-t-butylphenol	1.20	-	1.36	1.05-1.38	30	27
26	Dibenzofuran	1.60	-	1.64	1.47-1.89	10	4
27	2,4-Dinitrotoluene	0.35	-	0.32	0.24-0.42	32	1
28	2,4,5-Trichloroaniline	0.42	-	0.42	0.38-0.52	13	31
29	Fluorene	1.00	-	1.09	0.99-1.28	9	2
30	Diphenylamine	0.68	0.58	0.68	0.53-0.78	16	19
31	Azobenzene	0.24	-	0.24	0.18-0.40	26	6
32	Hexachlorobenzene	0.23	0.24	0.23	0.20-0.36	11	96
33	Pentachlorophenol	0.13	0.13	0.11	0.09-0.16	33	78

(continued)

TABLE 23. (Continued)

No.	Compound	Recommended RF	RF from Given Source(a)			%RSD of RF From Source B	a.m.u. Difference (b)
			A	B	C		
34	Phenanthrene	1.00	1.16	0.99	0.96-1.21	13	10
35	Anthracene	1.00	1.15	1.01	0.99-1.17	10	10
36	Acridine	0.60	-	0.61	0.59-0.91	7	9
37	Phenanthridine	0.70	-	0.67	0.65-0.92	6	9
38	Anthraquinone	0.30	-	0.29	0.26-0.41	8	4
39	Fluoranthene	1.00	-	0.98	0.16-1.16	12	10
40	2-Methylanthraquinone	0.25	-	0.25	0.22-0.33	4	10
41	Pyrene	1.00	-	0.97	0.93-1.23	11	10
42	Triphenylphosphate	0.20	-	0.20	0.17-1.83	10	86
43	Benzo(a)anthracene	1.00	1.11	1.08	0.87-1.26	17	16
44	Chrysene	1.00	1.02	1.03	0.80-1.29	8	12
45	Benzo(k)fluoranthene	1.00	1.10	1.05	1.07-1.20	12	12
46	Benzo(a)pyrene	1.00	1.00	0.99	0.91-1.07	15	12
47	Dibenzocarbazole	0.50	-	0.54	0.34-0.52	30	3
48	Indeno(1,2,3-CD) pyrene	0.80	0.45	0.80	0.64-0.88	18	12
49	Dibenzo(a,h)anthracene	0.60	0.58	0.60	0.48-0.70	19	14
50	Benzo(g,h,i)perylene	0.70	0.64	0.72	0.58-0.76	21	12

(a) A = FSCC QC Protocol prepared by Acurex for Drew Sauter of EMSL-LV.
B = Response factor study involving EMSL-LV, Raltech, and Battelle.
C = Range of values from calibration data reported by six laboratories participating in the interlaboratory study. (Data from two laboratories with sensitivity and tuning problems are not included.)

(b) Difference between quantification ion mass for listed compound and internal standard.

of the compounds listed, the percent RSD for response factors from the 3-laboratory study was 15-20% or higher.

The recommended ±40% range is based on using 2x RSD for compounds having RSDs of up to 20%. This range gives at least a 95% confidence level. The establishment of tighter RF limits at this time would be unrealistic. For example, the percent RSD obtained in the 3-laboratory study for benzo(a)anthracene was ±17%. This result would indicate that if a ±20% range was used there would be about a 30% chance of being outside the range.

The list of 50 compounds recommended for response factors monitoring was reviewed by EPA and was refined to 20 compounds as shown in Table 24. It is believed that the 20 compounds listed represent a range of compound polarities and response factors that will be adequate to monitor the analytical system. In addition, the use of 20 compounds rather than 50 compounds will aid cost effectiveness.

Calibration Standards

Eleven separate standard solutions labeled A through J were prepared for the Phase II and Phase III studies. The 140 semivolatile compounds to be used for calibration were prepared in four separate solutions (A through D) to minimize chemical reactions between components. The least soluble components were put in one solution, Solution A, at a concentration of 0.1 mg/ml for each component. The other three semivolatile calibration solutions were prepared at a five-fold or ten-fold higher concentration. The solutions were to be mixed and diluted just prior to use to give calibration solutions that contain 2, 10, 50, or 250 ng/µL of all 140 components. The components in Solution A, however, were not included in the high level mixture because of solubility limitations.

The semivolatile surrogate and internal standard compounds were prepared as solutions E and F, respectively. Volatile compounds used for standards were in solutions G, J, and K, and Supelco's Purgeable A, B, and C and were at concentrations of 0.2 mg/ml. These solutions were to be mixed and diluted to give calibration solutions suitable for adding 25, 100, 250 and 1000 ng of each compound to the purging apparatus.

A listing of the standard solutions is shown in Table 25. Seven of the volatile compounds listed in Solution G were not among the compounds to be quantified because they were found not to be purgeable. All of the semivolatile compounds except hexachlorophene, 2,4-D and 2,4,5-T were detected in the intralaboratory study.

Laboratory Selection

Laboratories were selected for participation in this program on the basis that each must have the GC/MS analytical instrumentation specified in the methods and must be staffed by persons experienced in GC/MS analysis of complex environmental samples. Ten laboratories were selected to provide bid requests. They were:

- Acurex
- Arthur D. Little, Inc.
- California Analytical Laboratories
- GCA Technology

TABLE 24. EPA RECOMMENDED COMPOUND RESPONSE FACTORS TO BE MONITORED DURING THE INTERLABORATORY COMPARISON STUDY

No.	Compound	Recommended RF	% RSD of RF From 3 Lab Study
1	Hexachlorobutadiene	0.14	19
2	Hexachloroethane	0.16	16
3	Hexachlorobenzene	0.23	11
4	2,6-Dichlorophenol	0.30	17
5	1,2,4-Trichlorobenzene	0.32	14
6	2,4-Dichlorophenol	0.34	19
7	2,4-Dimethylphenol	0.34	13
8	2,6-Dimethylaniline	0.40	10
9	Dibenzo(a,h)anthracene	0.60	19
10	N-Methylaniline	0.65	16
11	Diphenylamine	0.68	16
12	Benzo(g,h,i)perylene	0.70	21
13	Quinoline	0.70	11
14	Benzo(a)anthracene	1.00	17
15	Chrysene	1.00	8
16	Phenanthrene	1.00	13
17	Bis(2-chloroethyl)ether	1.10	17
18	Dimethyl phthalate	1.30	9
19	Dibenzofuran	1.60	10
20	Benzyl chloride	1.90	16

- Mead CompuChem
- Midwest Research Institute
- Southwest Research Institute
- Southern Research Institute
- Systems, Science, and Software
- West Coast Technical Services

Bid requests were sent to these laboratories and on the basis of the responses, four laboratories were requested to submit revised bids based on a work statement and analysis procedures both of which were modified as the result of questions from the ten initial respondents. The four laboratories GCA, Southwest Research Institute, Acurex, and Midwest Research Institute were subsequently accepted as subcontractors to Battelle to conduct the interlaboratory study work.

Five laboratories namely: Arthur D. Little, Mead CompuChem, Southwest Research Institute, California Analytical Laboratory and West Coast Technical Services were selected to participate and were funded through agreements

TABLE 25. LIST OF STANDARD SOLUTIONS

Semivolatile Calibration Solution A
(all compounds at 0.1 mg/ml in methylene chloride)

Aromatic Halocarbons

3,3'-Dichlorobiphenyl
4,4'-Dichlorobiphenyl
2,2'-4,4'-Tetrachlorobiphenyl
2,2'-4,4',6,6'-Hexachlorobiphenyl

Aromatic Hydrocarbons

Benzo(a)anthracene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene

Aromatic Hydrocarbons (con't)

Indeno(1,2,3-cd)pyrene
Chrysene
Benzo(a)pyrene
Dibenzo(a,h)anthracene

Amines

1,2,7,8-Dibenzocarbazole

Semivolatile Calibration Solution B
(all compounds at 1.0 mg/ml in benzene)

Aromatic Hydrocarbons

Naphthalene
1,2,4-Trimethylbenzene
1,2,4,5-Tetramethylbenzene
Biphenyl
Acenaphthylene
Acenaphthene
2-Methylnaphthalene
2-Ethylnaphthalene
2,3-Dimethylnaphthalene
1,2,3,4-Tetrahydronaphthalene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene

Amines

Aniline
4-Chloroaniline
4-Bromoaniline
2-Nitroaniline
3,4-Dichloroaniline
2,4,5-Trichloroaniline

Amines (con't)

3-Nitroaniline
4-Chloro-2-methylaniline
4-Nitroaniline
2,6-Dichloro-4-nitroaniline
2-Chloro-4-nitroaniline
2,4-Dinitroaniline
N-Methylaniline
4-Chloro-2-nitroaniline
4-Methylaniline
2,6-Dimethylaniline
4-Aminobiphenyl
1-Aminonaphthalene
N,N-Dimethylaniline
Phenanthridine
4-Methylpyridine
2,4-Dimethylpyridine
4-t-Butylpyridine
2,4,6-Trimethylpridine
Quinoline
4-Methylquinoline
Acridine
Carbazole
3,3'-Dichlorobenzidine
Diphenylamine

(continued)

TABLE 25. (Continued)

Semivolatile Calibration Solution C
(all compounds at 0.5 mg/ml in methylene chloride)

Aliphatic Halocarbons

1,4-Dichlorobutane
Pentachloroethane
Hexachloroethane
Hexachloropropene
Hexachlorobutadiene

Aromatic Halocarbons

4-Chlorotoluene
Bromobenzene
1,2-Dichlorobenzene
1,4-Dichlorobenzene
1,2,4-Trichlorobenzene
1,2,4,5-Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene
Benzal chloride
Benzyl chloride
1-Chloronaphthalene
2-Chloronaphthalene
α,α,α-Trichlorotoluene

Aromatic Nitro Compounds

Nitrobenzene
1,3-Dinitrobenzene
2-Nitrotoluene
4-Nitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,-Chloro-4-nitrobenzene
2,4-Dinitrochlorobenzene

Phenols

2-Chlorophenol
2-Nitrophenol
Phenol
2,4-Dimethylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol

Phenols (con't)

4-Chloro-3-methylphenol
2-Methylphenol
4-Methylphenol
Thiophenol
4-Chlorophenol
2,6-Dichlorophenol
2,4,5-Trichlorophenol
Hexachlorophene
4-Hydroxybiphenyl
2-Naphthol
4-t-Butylphenol
2-Chloro-4-nitrophenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
Pentachlorophenol
4-Nitrophenol
2,6-Di-t-butyl-4-methylphenol
2,4-Di-t-butylphenol
Diethylstilbestrol

Chlorinated Pesticides

4,4'-DDD
4,4'-DDE
4,4'-DDT
Methoxychlor
Trifluralin
Pentachloronitrobenzene

Acids

4-Chlorobenzoic acid
Benzoic acid
4-Bromobenzoic acid
2,4-Dichlorophenoxyacetic acid
2,4,5-Trichlorophenoxyacetic acid

Haloethers

Bis(2-chloroethyl)ether
Bis(2-chloroethoxy)ethane
4-Chlorophenyl phenyl ether

(continued)

TABLE 25. (Continued)

Semivolatile Calibration Solution D
(all compounds at 1.0 mg/ml in methylene chloride)

Phthalates

Dimethyl phthalate
Di-n-butyl phthalate
Di(2-ethylhexyl) phthalate

Phosphates

Tri(p-tolyl) phosphate
Triphenyl phosphate

Aldehydes

Benzaldehyde
4-Chlorobenzaldehyde

Ethers and Sulfides

Anisole
Phenyl ether
Dibenzofuran

Ketones

Anthraquinone
2-Methylanthraquinone
Propiophenone
Acetophenone

Miscellaneous

Azobenzene
Acetanilide
Benzyl alcohol
Di(2-ethylhexyl) sebacate

Semivolatile Surrogate Standard Solution E
(all comppunds at 10 mg/ml in methylene chloride)

Decafluorobiphenyl
2-Fluoroaniline
Pentafluorophenol

Semivolatile Internal Standard Solution F
(all compounds at 200 μg/ml in methylene chloride)

D_5-Bromobenzene
D_8-Naphthalene
D_{10}-Phenanthrene
D_{10}-Biphenyl
D_{10}-Acenaphthene
D_{10}-Pyrene
D_{12}-Chrysene
D_{12}-Benzo(a)pyrene
D_5-Aniline
D_5-Phenol
D_5-Nitrobenzene
D_3-2,4-Dinitrophenol
Decafluorotriphenylphosphine

(continued)

TABLE 25. (Continued)

Volatile Calibration Solution G
(all compounds at 0.2 mg/ml in methanol)

2-Chloroethylvinyl ether
1,1,2-Trichlorotrifluoroethane
Dibromomethane
Allyl chloride
Ethylene dibromide
Chloropicrin
2-Chloropropane
1-Chlorobutane
o-Xylene
Styrene
2-Butanone
Cyclopentanone
4-Methyl-2-pentanone
2-Hexanone
Carbon disulfide
Dimethyl disulfide
Epichlorohydrin
2-Chloroacrylonitrile
Acetonitrile
Dichloroacetonitrile
n-Propionitrile
Chloroacetaldehyde
2-Chloroethanol
N-Nitrosodimethylamine
Vinyl acetate
Dimethyl sulfide
Diethylether
Acetone
Methyl chloroacetate
Methyl acrylate
Methyl methacrylate

Volatile Surrogate Standard Solution H
(all compounds at 10 mg/ml in methanol)

1,2-Dibromotetrafluoroethane
Bis(perfluoroisopropyl) ketone
Fluorobenzene
m-Bromobenzotrifluoride

Volatile Internal Standard Solution I
(all compounds at 0.2 mg/ml in methanol)

D_4-1,2-Dichloroethane
D_6-Benzene
D_5-Ethylbenzene
4-Bromofluorobenzene

Volatile Calibration Solution J
(all compounds at 0.2 mg/ml in water)

Acrolein
Acrylonitrile

(continued)

TABLE 25. (Continued)

Volatile Calibration Solution K

2-Chloroethyl vinyl ether	0.2 mg/ml in tetraglyme

Supelco's Purgeable A
(all compounds at 0.2 mg/ml in methanol)

Methylene chloride
1,1-Dichloroethene
1,1-Dichloroethane
Chloroform
Carbon tetrachloride
1,2-Dichloropropane
Trichloroethylene
1,1,2-Trichloroethane
Dibromochloromethane
Tetrachloroethene
Chlorobenzene

Supelco's Purgeable B
(all compounds at 0.2 mg/ml in methanol)

trans-1,2-Dichloroethene
1,2-Dichloroethane
1,1,1-Trichloroethane
Bromodichloromethane
trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
Benzene
Bromoform
1,1,2,2-Tetrachloroethane
Toluene
Ethylbenzene

Supelco's Purgeable C
(all compounds at 0.2 mg/ml in methanol)

Chloromethane
Bromomethane
Vinyl chloride
Chloroethane

directly to EPA. From among the laboratories that volunteered to participate in the interlaboratory study, two were selected; these laboratories are Environment Canada and Battelle Northwest Laboratories but these laboratories eventually declined participation in the study.

Names and addresses of the participating laboratories follow:

Acurex Corporation
405 Clyde Avenue
Mountain View, California 94043
Contact: Viorica Lopez-Avila
Telephone: (415) 964-3200

Arthur D. Little, Incorporated
20 Acorn Park
Cambridge, Massachusetts 02140
Contact: Linda Sadowski
Telephone: (617) 864-5770

California Analytical Laboratories
5895 Powrer Inn Road
Sacramento, California 95824
Contact: Mike Miille
Telephone: (916) 381-5105

GCA Corporation
Technology Division
213 Burlington Road
Bedford, Massachusetts 01730
Contact: Gary Hunt
Telephone: (617) 275-5444

Mead-CompuChem
P.O. Box 12652
Research Triangle Park,
North Carolina 27709
Contact: Paul Mills
Telephone: (919) 549-8263

Midwest Research Institute
425 Volker Boulevard
Kanas City, Missouri 64110
Contract: Jim Spigarelli
Telephone (816) 753-7600

Southern Research Institute
2000 Ninth Avenue South
Brimingham, Alabama 35205
Contract: Ruby James
Telephone: (205) 323-6592

Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78238
Contact: Carter Nulton
Telephone: (512) 684-5111

West Coast Technical Services
Incorporated
17605 Fabrica Way
Cerritos, California 90701
Contact: Rich Amano
Telephone: (213) 921-9831

Environment Canada
Laboratory Services Division
Air Pollution Technology Center
River Road Laboratories
Ottawa, Ontario K1A 1C8
Contact: Judy Lockwood
Telephone: (613) 998-3671

Battelle
Pacific Northwest Laboratories
Battelle Boulevard
Richland, Washington 99352
Contact: Don Schoengold
Telephone: (509) 376-0005

QUALITY ASSURANCE/QUALITY CONTROL

The objective of Quality Assurance (QA)/Quality Control (QC) activities conducted for any chemical analysis program is to provide data of known quality. In case the results of analyses are contested in any way, the quality of these data must be demonstrable.

While the data from this study are not likely to be directly contested in a pollution assessment case, the validity of the method may be contested and does need to be substantiated. The results of this study will form the basis for quality control requirements when the method is applied routinely.

QA Objectives

The objectives of QA/QC activities in the interlaboratory test were to make certain that the laboratory work conducted to evaluate the chemical analysis methods was done under controlled conditions, that those controls were uniformly applied by all collaborators and that all experimental work was recorded for archival storage.

In addition, when the analysis method is fully evaluated and is applied for routine analyses of hazardous wastes, the method description will include the necessary and appropriate quality control elements and requirements. Part of the requirements for that quality assurance and quality control will be based on experience and knowledge derived from this evaluation. Therefore, it is expected that all persons involved in this program will be aware of the ultimate use of the methods and will be alert, sensitive and critical to controls instituted to provide high quality data.

Quality Control - Performance Criteria and Checks

Quality control activities start with a description of the method which must be followed without exception. Before any laboratory work, the method must be read and understood by all personnel who use it. Questions regarding what is to be done in the interlaboratory test must be discussed with Battelle persons before laboratory work starts. In that way uncertainties can be corrected or clarified among all cooperating laboratories and all will possess the same information prior to analysis. Thus, to the extent possible, the collaborators will conduct all operations in exactly the same manner.

Control was maintained by monitoring the mass spectrometer tuning (using DFTPP or BFB), and analyzing process blanks and calibration standards. The details of the required quality control measures are described in the methods and in the QC Protocol for Fused Silica Capillary Columns.

In application of the methods it was expected that care was exercised to use properly calibrated and clean apparatus such as balances and volumetric glassware for extract preparation and to ascertain that the GC/MS system was functioning properly.

On-Site Audits and Performance Evaluation Samples

After the study participants received and reviewed the instruction manual each laboratory underwent two audits. The first was a systems audit conducted at each laboratory to ascertain that the facilities necessary to conduct the study were available and to review the instruction manual. If there was any misunderstanding of the manual by one or more laboratories, clarifications were distributed to all participants before the study continued.

The second audit consisted of performance evaluation samples analyzed by each participant. This exercise not only provided laboratory qualification but offered another opportunity to clarify misunderstandings and correct unclear statements in the instruction manual and gave an excellent opportunity for participants to become intimately familiar with the test methods.

GC/MS Run Logs

Several forms were supplied for reporting analytical information and a log of GC/MS runs. A separate log (Forms 1V and 1S) was required for each mass spectrometer used to determine volatile compounds and for each mass spectrometer used to determine semivolatile compounds. Run numbers should be consecutive from the very first calibration run to the last sample or calibration run. We intend that the analysis runs for this program be consecutive and without interruption by other programs.

GC/MS Calibration

The daily run routine must include at least one calibration run at the beginning of the day and additional calibration runs during the day if more than 8 sample runs were made in one day.

Surrogate Standards

All samples must be spiked with surrogate compounds before extraction. The surrogate compounds are:

For Volatile Compounds

1,2-Dibromotetrafluoroethane
Bis(perfluoroisopropyl) ketone
Fluorobenzene
m-Bromobenzotrifluoride

For Semivolatile Compounds

Decafluorobiphenyl
2-Fluoroaniline
Pentafluorophenol

The spiking level used should be that which gave a concentration in the final extract used for GC/MS analyses that was equal to the level of the internal standard added, assuming 100% recovery. This level was determined as described in Section 8.4 of the methods. Thus two aliquots of each sample must be screened, one for volatile compounds and one for semivolatile compounds, before aliquots can be spiked with surrogates and analyzed.

Blanks

Blanks were defined as system or process blanks and consisted of all reagents used in sample preparation and carried through the entire preparation process and finally analyzed by GC/MS. This activity assessed the purity of reagents and cleanliness of apparatus and environment. It was required that a system blank be generated and analyzed with every batch of samples prepared or with every new batch of reagent material. A minimum of two process blanks for the volatile analyses and two process blanks for the semivolatile analyses must be run and the data reported.

Documentation and Records

The documents for this program include the Manual of Instructions for collaborators of which this QA/QC plan was a part, the Program Review Inquiry form, data reports, letters of transmittal,pertinent records of telephone conversations and all data and records associated with this program. Copies of these documents will be kept on file by Battelle for audit purposes and for possible submission to the EPA at the conclusion of the study.

A record shall be kept by participants of all efforts and events associated with the laboratory work and of all data such as:

- Sample Handling

  Date received
  Volume and/or weight of samples
  Condition of samples
  Location and temperature of storage
  Date removed from and returned to storage

- Analytical Data

  Date of extraction and GC/MS analysis
  All volumes and weights used
  Dilution and concentration factors
  Amount of internal standard added
  Internal standard area response
  Injection volume
  Relative response factors used for quantification
  Total solvent extractable content

Major volatile compounds content
Scan number
Absolute and/or relative retention time
Most intense ions
Compound identification
Probable molecular weight
Total ion current chromatograms
Library search results
9-Track tape files
Search system used
Calibration results
Mass spectrometer tuning results
Maintenance records

Most of the above information is "required data" to be reported on forms supplied or in specified format. The deliverables required from each participating laboratory are as follows:

- Amount, absolute retention time, relative retention time, and response factor used for each of the target (up to 200) compounds found in each of three replicates of 10 waste samples at levels greater than 0.02 times the level of internal standard used.
- Amount, tentative identification most intense ion, absolute retention time and relative retention time for each of the 20 major volatile compounds and the 20 major semivolatile compounds found in each of the three replicates of 10 waste samples (some or all of these may be among the list of 200).
- Relative ion abundances found in each GC/MS run (including blanks, calibration runs and sample runs) for the tuning compound (BFB or DFTPP) included in the internal standard solution.
- Peak area counts found for D_6-benzene or D_{10}-phenanthrene in each GC/MS run.
- Relative retention times and response factors found for each of the 200 compounds in initial GC/MS calibration runs using Battelle-supplied calibration solutions.
- Relative retention times and response factors found for each of 20 volatile compounds and each of 80 semivolatile compounds in each GC/MS calibration run using Battelle-supplied calibration solutions.
- Percent recovery of three surrogate compounds spiked into each replicate analyzed.
- The total ion chromatogram (8-1/2 x 11) from each GC/MS run with a scan number scale indicated and the internal standard peaks and surrogate standard peaks indicated.

- The enhanced mass spectrum and library search results (each on one 8-1/2 x 11 page) for each compound reported that is not on the list of 200 compounds.

- A narrative description of the GC/MS system used to acquire data and the computer software and/or manual processes used to obtain the qualitative and quantitative results reported.

- A completed program review inquiry to critique the methods and indicate where clarifications, modifications, or additional specifications would be useful in the methods.

- In addition to the above, all of the GC/MS raw data must be archived on 9-track tape for a period of one year.

Performance criteria associated with these functions have been established for the interlaboratory test phase of the program and are a part of the instruction manual.

QC For Fused Silica Capillary Columns

A QC Protocol for fused silica capillary columns was developed by Acurex under the direction of Mr. Drew Sauter, EPA-LV and modified by Battelle for application to this interlaboratory study. This protocol for the use of fused silica capillary columns must be followed when the method for the determination of semivolatile organic compounds was used. No deviations from this protocol were permitted. This protocol (revision as of July 1982) is presented in Appendix A.

Quantification Limits

The method descriptions cite an ideal detection limit of 1 ppm with higher limits expected for complex samples. However, there was a need to cite detection limits for defensibility of data.

Although a study of quantification limits has been conducted on a separate contract with EMSL-Cincinnati, some additional comments regarding quantification limits that can be expected may be helpful at this time. For the purposes of this discussion, we assume that detection limit means quantification limit. As stated in the methods under the section on Scope and Application, the detection limit is approximately 1 µg/g but proportionately higher for samples that contain more than 1 mg/g of total solvent extractable material (semivolatiles method) or total volatile material (volatiles method). This estimated quantification limit is based on the premise that the amount of the primary internal standard used was 50 times the lowest amount that can be quantified. Thus, in the method for semivolatiles, in which 50 µg/ml of D_{10}-phenanthrene was used as the primary internal standard, the lowest amount that can be quantified was taken as 1 µg/ml which would be 1 ng injected. For samples containing 1 mg/g or less of total solvent extractable content (TSEC), the extract from 1 g of the waste would be concentrated to 1 ml (to give a solution containing 1 mg TSEC/ml) and treated with 50 µg of internal standard. Thus, the internal standard would be present at a level representing 50 µg/g of waste and the quantification limit would be 1 μg/g. If the sample contained 100 mg/g of TSEC, the extract from 0.01 g of the waste would be diluted to 1 ml (to give a solution containing 1 mg TSEC/ml) and treated with 50 μg of the internal standard. In this case, the internal standard would be at a level representing 5000 μg/g of waste and the quantification limit would be 100 μg/g.

The quantification limit is based on the lowest mass spectrometer response that can be quantified. If a Finnigan 4000 is used and an area of 100,000 is obtained for 50 ng of D_{10}-phenanthrene, the above rationale means that an area of 2000 is being taken as a practical quantification limit in a complex sample matrix. The rationale also implies that the quantification limit of a compound of interest will vary with its response factor relative to D10-phenanthrene. Thus, if the response factor of a compound relative to D10-phenanthrene is 0.1, the area obtained would be 10 times lower and the quantification limit would be 10 times higher.

The following formula may be used for estimating the quantification limit of the method when applied to the determination of a particular compound in a particular waste:

$$\text{Quantification Limit, }\mu\text{g/g} = \frac{1}{\text{RF rel. to } D_{10}\text{-phen}} \text{ X TSEC, mg/g.}$$

A similar treatment of the method for volatiles leads to a similar formula in which D6-benzene is the primary internal standard and total volatile content (TVC) is used to determine the volume of extract analyzed:

$$\text{Quantification Limit, }\mu\text{g/g} = \frac{1}{\text{RF rel to } D_{6}\text{-benzene}} \text{ X TVC, mg/g.}$$

The above formulas provide reasonable but sometimes conservative estimates of the quantification limits. For example, in some cases, the concentration of the extract analyzed may be 10 times greater than that considered in the above calculations and result in a quantification limit that is 10 times lower than the estimate given by the formulas.

PROPOSED ADDITIONAL STUDIES

During the course of conducting the Phase II studies and reviewing the performance evaluation data from Phase III, several additional studies that would strengthen the overall program have become apparent to us. Some of the additional studies that would benefit the program, e.g., homogeneity of the spiked wastes, quantification limits of the methods, comparison of the tetraglyme method to direct purge and trap methods, methyl t-butyl ether as an extraction solvent, and extract matrix effects, have been discussed previously and were conducted on other contracts. Additional studies recommended are discussed below.

DFTPP Stability

In order to determine whether the mass spectrometer tuning meets the EPA criteria for use in the determination of semivolatile compounds, DFTPP must be introduced to the mass spectrometer via the gas chromatograph. This GC/MS analysis is generally made as a separate run at the beginning of each day prior to the analysis of calibration samples. In the method prepared for the collaborative study, DFTPP was specified to be included in the internal standard solution and to be analyzed in every run. With this protocol the DFTPP check of tuning could be conducted as part of the first calibration run of the day and thereby decrease the time and costs involved. Unfortunately, DFTPP solutions frequently degrade within a few days, so that the resulting DFTPP mass spectrum obtained is too weak to give good relative ion abundance data. When DFTPP is analyzed by itself, a fresh solution is frequently prepared every few days to avoid the degradation problem. It is not practical to prepare fresh multicomponent internal standard solution or calibration solutions containing DFTPP every few days. The multicomponent internal standard solution containing DFTPP that was prepared for the program was found to be stable for several months at room temperature when stored in sealed glass. After the ampoules were opened, the DFTPP seemed to decompose in a few days at variable rates. The instability of DFTPP is very likely caused by an air oxidation of the phosphine to the phosphine oxide. It may be possible to stabilize DFTPP solutions by the addition of an oxygen scavenger. In order to be of use, the oxygen scavenger must not interfere with the GC/MS analysis, which in general means that it should be either nonvolatile or very volatile. Two volatile compounds that may serve as effective oxygen scavengers and DFTPP stabilizers are triethylphosphine and trimethyl phosphite.

Because of the time and cost advantages to be gained by incorporating the DFTPP tuning check with a calibration run, it is recommended that DFTPP stability and the effectiveness of oxygen scavengers be studied.

Improved Internal Standard Solution

The internal standard solution that has been prepared for the collaborative study contains eight deuterated compounds as internal standards, four deuterated polar compounds as column performance standards, and DFTPP. It has been found that one of the compounds originally suggested as an internal standard, D_{10}-biphenyl, cannot be used in the study because of the frequent interference of a coeluting compound, 1-chloronaphthalene. Because of the interference, neither D_{10}-biphenyl or 1-chloronaphthalene can be quantified reliably. In addition two column performance compounds in the internal standard solution, namely D_5-phenol and D_5-aniline, occasionally coelute and cannot be quantified reliably. In order to improve the usefulness of the internal standard solution it is recommended that D_{10}-biphenyl be deleted as an internal standard and that D_3-2,4-dichlorophenol and D_9-2-aminobiphenyl be used in place of D_5-phenol and D_5-aniline as column performance standards.

The above change will permit D_5-phenol to be available as an acidic surrogate. In general, fluorinated compounds instead of deuterated compounds were selected as surrogates because many of the more common deuterated compounds were desired as internal standards and because many of the other deuterated compounds available were too expensive. In many cases, as much as 20 to 50 mg of surrogate is required for the 3-gram sample analyzed. Although most of the deuterated compounds available that are not used as internal standards would be too costly, D_5-phenol, D_7-quinoline, and D_8-Fluorene cost less than $10/50 mg and would be suitable as acidic, basic, and neutral surrogates, respectively.

It is recommended therefore, that the deuterated compounds discussed above be studied in respect to potential interferences and, if found suitable, be used in the remainder of the interlaboratory study. It will also be of interest to study the usefulness of including additional compounds to monitor the mass spectrometer tuning, e.g., pentafluorobromobenzene, octafluoronaphthalene, or trichlorotrifluorobenzene.

Gas Chromatography of Pyridines

Four pyridines have been included in the list of representative semivolatile compounds selected for the interlaboratory study. Even though the pyridines are relatively low boiling, they usually give very broad peaks under the GC conditions used. Frequently there are two or more humps to the peaks which indicate that the pyridines may be released from different salts in the injection port at different rates, e.g. from salts with 2,4-D, 2,4,5-T, chlorobenzoic acid, etc., which are included in the solutions. It has also been noted in other work that the pyridine peak becomes much narrower if the injector temperature is decreased. This latter observation may indicate a reaction of the pyridine with the methylene chloride solvent to form a hydrochloride salt from which the pyridine is slowly released. It is recommended that studies using other solvents, e.g., methyl t-butyl ether, and studies of the effects of adding various acidic compound be conducted to improve the chromatography of pyridines. The results may have a significant bearing on the reliability of data from the quantification of both acids and bases. It may be that the recommended GC/MS conditions are not suitable for the simultaneous determination of some acids and bases. It may be found that methylene chloride is not suitable as a solvent for compounds as strongly basic as pyridines.

Tetraglyme Method Interferences

Potentially interfering peaks can be obtained when the tetraglyme method is used for the determination of purgeable compounds. Most of these peaks of concern come from impurities in the tetraglyme while others may come from antifoam agents used. When large aliquots of tetraglyme extracts are used, significant amounts of tetraglyme may purge, foam, or both from the water and show up as a very broad peak several runs later. It is recommended that tetraglyme purification, tetraglyme substitutes, and antifoam agents be studied to improve the tetraglyme procedure. Tetraglyme purification would involve fractional distillation or prolonged sparging at an elevated temperature. A chemical supply house may be willing to provide purified tetraglyme. A sparging procedure and the use of antifoams is being evaluated for the Cincinnati hazardous waste program.

As far as a tetraglyme substitute is concerned, any solvent of interest will need to be less volatile than tetraglyme and contain lower levels of purgeable impurities than tetraglyme but retain all of the advantages of tetraglyme; namely low viscosity, water-miscibility, oil-miscibility, and availability. Some potential candidates as tetraglyme substitutes are hexaglyme, triethylene glycol propionate, 15-crown-5 ether, and 18-crown-8 ether. Sources of such compounds have been investigated.

On-Column Injection

Variable injector discrimination can occur when the usual split or splitless injection technique is used in capillary column GC work. The variable discrimination leads to variable quantitative results. Injector discrimination can be avoided by using on-column injection. Various on-column injectors for capillary column work are now available and their use is becoming more common. In addition to avoiding injector discrimination, on-column injection decreases compound degradation that may occur in the injector and cause poor precision and accuracy. It is recommended that a comparison of the precision and accuracy of on-column injection versus splitless injection be made using extracts of the spiked waste samples being studied in the interlaboratory program. After completion of this project, such a study was reported in J. Chromatogr. Sci. 21, 512, 1983. Although it would not be practical to require the participating laboratories to switch to on-column injection at this point, the information obtained from the comparison study could be very useful in future hazardous waste analysis programs.

Re-Analysis of Samples to Determine Semivolatile Compounds

Intralaboratory data recently collected at Battelle with the revised method were better than the data collected in September. The extractions of the six spiked wastes for the determination of semivolatile compounds in the intralaboratory study were conducted last fall using the first generation method. That method involved the use of a Polytron homogenizer. The method was later revised to use sonification. In order to strengthen the background data base for justification of the initiation of Phase III it is recommended that the six spiked waste samples be extracted and analyzed in triplicate at Battelle using the revised method.

Statistical Evaluation of Data

The Phase III program as originally proposed includes a statistical evaluation of the amounts of individual compounds found in the eleven ILS samples by the ten participating laboratories. The data involved are those to be reported on Form 2 and 3, i.e., amounts of listed and unlisted compounds. However, a large body of additional information has been requested that may provide explanations to variabilities encountered. This additional information includes area and retention time of the primary internal standards, D_6-benzene or D_{10}-phenanthrene, relative ion abundances of DFTPP or BFB, retention times and response factors of internal standard components, surrogate recovery data, retention times or relative retention times of all compounds in all calibration runs, and response factors of all compounds in all calibration runs. Some of this additional information from the performance evaluation runs has already been evaluated to a limited extent. It is recommended that a more thorough evaluation be made of these additional data from the performance evaluation runs and from the remainder of the study.

REFERENCES

1. Federal Register Monday, December 18, 1978, Part IV, Vol. 43, No. 243 p. 58956.
2. ASTM, Annual Book of Standards, 1981, Part 41, p. 964.
3. ASTM Standards on Precision and Accuracy for Various Applications 1st Ed. 1977.
4. Final Report on Residual Waste Analyses to EPA, March 31, 1981, Contract 68-02-3628, Battelle.

Phase III Studies

INTRODUCTION

The Environmental Protection Agency, under the authority of the Resource Conservation and Recovery Act of 1976, is charged with the responsibility of assessing the potential hazard of municipal and industrial solid wastes. One of the characteristics of a waste that must be determined in order to assess the potential hazard associated with the disposal of the waste, is the organic chemical content. A variety of analytical methods have been developed and applied to the determination of organic constituents in solid waste. Each research group associated with the development of a given method instituted appropriate intralaboratory quality control to determine the applicability, accuracy and precision of the method developed. However, none of the methods has been evaluated by conducting a well-designed interlaboratory comparison study. The interlaboratory collaborative study conducted by Battelle involved three phases:

I Methods Evaluation, Modification and Selection
II Intralaboratory Evaluation and Methods Revision
III Interlaboratory Evaluation

The objective of Phase I was the selection of two methods using combined gas chromatography/mass spectrometry (GC/MS) for the analysis of solid wastes, one method for determination of volatile organic compounds and one method for determination of semivolatile organic compounds. The results of the Phase I effort were presented in the Phase I Report dated July 14, 1981 (1). The objective of Phase II was the single laboratory application, critical review and revision of the methods selected in Phase I. Phase II also included the development of a protocol for conducting the interlaboratory collaborative study. The results of the Phase II effort were presented in the Phase II report dated September 24, 1982 (2).

The objective of Phase III, the subject of this report, was the performance of a collaborative study to assess the precision and accuracy of the revised methods that resulted from Phase II research efforts. The collaborative study involved triplicate analyses of seven different spiked waste samples by nine participating laboratories using the two revised GC/MS analysis methods. The data were used in a statistical analysis to determine the between-laboratory and within-laboratory components of the total variability.

CONCLUSIONS

Phase I

- Gel permeation chromatography was of marginal value and was not necessary because industrial wastes generally do not contain high molecular weight substances,
- Homogenization of wastes can in most cases be carried out through use of a Brinkmann Polytron Homogenizer although sonication was the ultimate method of choice,
- Fused silica capillary columns were recommended for GC/MS studies and have been specified in the methods description.

Phase II

- Tetraglyme was found to be superior to polyethylene glycol as the solvent for extraction of volatile organic compounds because of lower viscosity and better solvent properties.
- Ultrasonic energy was found to be superior to mechanical energy for dispersing a sample in methylene chloride for extraction of semivolatile compounds.
- The methods selected in Phase I were, with the above modifications, found to be suitable for use in Phase III.
- The methods are adequate but some additional work is suggested as follows:

  Stability of DFTPP and the effectiveness of oxygen scavengers to stabilize DFTPP should be studied.

  Because of interferences in the use of the recommended internal standard compounds (for semivolatile compounds) the use of other internal standards should be studied in respect to interferences.

  To improve chromatography of pyridines and based on observations made during Phase II studies, it appears beneficial to investigate the usefulness of solvents other than methylene chloride.

  Potentially interfering peaks were frequently obtained when the tetraglyme method was used for the determination of purgeable compounds. Tetraglyme purification, tetraglyme substitutes and antifoam agents need to be studied to improve the procedure.

The precision and accuracy obtained using on-column injection versus splitless injection should be compared.

The means suggested to calculate detection limit provides a conservative estimate of quantification limits. Some work was needed to provide a rigorous, yet simple means, for estimating detection and quantification limits.

Phase III

- Sample-to-sample variations were evident for both analysis procedures.
- Precisions of relative retention times for semivolatiles were excellent (average of 1.9%).
- Precisions of retention times for volatiles were good (average of 18%).
- Response factor relative standard deviations were less than 40% for SVs and ranged from 15 to 80% for VOAs.
- Laboratory-to-laboratory variability was evident for the total number of compounds detected.
- Within laboratory component of the spike recovery variability averaged about 30% for both volatiles and semivolatiles.
- Between laboratory component of the variability was about twice the within laboratory component for both volatiles and semivolatiles.
- Seventy percent of the potential positive results of high level spike data were reported compared to 50 to 60 percent of potential low level spike data.
- Tetraglyme VOA method gave best results for high boiling compounds and poorer results for more polar compounds.
- Semivolatile method gave best results for aromatic hydrocarbons and halocarbons and poorer results for benzoic acids and nitrophenols.

The most striking difference in the interlaboratory application of the two analysis methods was evident for the screening phase of both protocols. The amount of tetraglyme extract used for the purge and trap analysis varied as much as three orders of magnitude. The concentration factor used for the semivolatile methylene chloride extract also varied by as much as three orders of magnitude. Interpretation of instructions for these decisions by each of the participating laboratories should be examined.

The quantity and type of organic compounds found for each of the waste samples indicated that some of the samples could have undergone change with time. More time elapsed between preparation of spiked samples and analysis than planned in the experimental design. Performance evaluation samples were analyzed by each of the participating laboratories to provide evidence of capability. The planned time of three weeks for this event was exceeded by a factor of 3. The time originally planned for interpretation of Performance Evaluation data was also exceeded since it was necessary to evaluate a number of factors prior to approval by EPA to initiate Phase III activities. Finally, the Phase III interlaboratory results were requested in two months, however, four months were required by the participants due to both scheduling and contractual difficulties. The primary technical problem was the purity of tetraglyme required by the VOA protocol. The tetraglyme batch used by Battelle in the Phase II developmental work did not cause interferences. Some of the other laboratories could not obtain sufficiently pure tetraglyme for Performance Evaluation sample analysis causing time delays. EMSL-LV arranged for pure tetraglyme, supplied by Radian, to be made available for Phase III of the study.

Examples of suspected sample degradation include ILS-5 and ILS-6 which contained fewer volatile organic constituents than originally found. Also degradation of DDT and absence of nitro compounds were observed for ILS-6.

RECOMMENDATIONS

Further examination of certain results and observations of the collaborative study for evaluation of hazardous waste methodology will significantly enhance the value of this complex study. The volume of data generated probably far exceeds data obtained for any previous interlaboratory method evaluation. The scope of the study covered statistical evaluation of only a small portion of this data base. In addition, no provisions were included for statistical reanalysis excluding outlier results. Based on the interpretation of the analytical data the following recommendations were presented for consideration:

- Expand the volume of statistically analyzed data to include further analysis of data to identify observed variances.
- Repeat statistical analysis of percent recovery data excluding obvious outliers.
- Investigate sources of significant variability such as
  - -- Prescreening
  - -- Extraction
  - -- Instrumental Analysis
  - -- Response factor determination
  - -- Confirmation of compound identification and quantification procedures
  - -- Calculation
- Conduct in-depth interview at collaborators laboratories to evaluate interpretation of instructions (both excellent and poor performances would provide valuable insight).
- Modify method instructions and quality control protocols to eliminate potential sources of variance where possible.
- Investigate and confirm suspected sample degradation for ILS-5 and ILS-6.

The conduct of the tasks recommended above will result in a more thorough evaluation of the data generated by the collaborative study. It is anticipated that the revised comparative statistics will be significantly improved in terms of precision and accuracy. Further, the resulting revisions in the protocols for volatile and semivolatile organic analysis will result in more uniform application of these methods in future EPA analysis programs. Many of the recommendations are being implemented on U.S. EPA Contract No. 68-03-3122 by the EMSL-CIN.

EXPERIMENTAL PROCEDURES

ANALYTICAL TEST PROCEDURE

Two analytical test procedures were evaluated in the interlaboratory study. One of the procedures was a GC/MS analysis procedure for the determination of volatile organic compounds. The procedure involved the extraction of a waste sample with tetraethyleneglycol dimethyl ether (tetraglyme), the addition of a portion of the extract to water, and analysis by the purge and trap technique of EPA Method 624 (3). The other method, a GC/MS analysis method for the determination of semivolatile organic compounds, involved the extraction of the waste by sonification with methylene chloride under neutral conditions in the presence of anhydrous sodium sulfate, and GC/MS analysis of the extract using a fused silica capillary column. Complete descriptions of the two methods are given in Appendix A and Appendix B. A quality control protocol for GC/MS analyses involving fused silica capillary columns was specified as a supplement to the method for the determination of semivolatile organic compounds. The quality control protocol was based on a protocol developed by Acurex for EMSL-Las Vegas and was revised by Battelle for applicability to the collaborative study. The revised protocol is presented in Appendix C.

COLLABORATIVE TEST PROCEDURES

Preparation of Calibration Solutions

All of the standard solutions required for the study were purchased or prepared by Battelle in sealed glass ampoules and distributed to the participating laboratories. The standards included standard calibration solutions, surrogate recovery standard solutions, and internal standard solutions. The standard solutions distributed for the determination of volatile compounds included six calibration solutions containing a total of 53 representative volatile compounds, a surrogate solution containing four fluorinated compounds as recovery standards, and an internal standard solution containing bromofluorobenzene as a mass spectrometer tuning standard and three deuterated internal standards. The standard solutions distributed for the determination of semivolatile compounds included four calibration solutions containing a total of 140 representative semivolatile compounds, a surrogate solution containing three fluorinated recovery standards, and an internal standard solution containing decafluorotriphenylphosphine as a mass spectrometer tuning standard and twelve deuterated internal standards and GC/MS performance standards. The compositions of the standard solutions are given in Appendix D.

Preparation of Spiked Wastes

The wastes used for the study were selected to challenge the extraction procedure and to represent a broad range of waste types. The wastes are listed in Table 1. Each waste was spiked with the 9 representative volatile compounds and 36 representative semivolatile compounds listed in Table 2. The concentrations spiked into the wastes are given in Tables 3 and 5 showing the volatile and semivolatile compounds, respectively. These spike concentrations were chosen to be similar to the levels of other volatile and semivolatile components present in the unspiked wastes. Most of the spiked compounds were different from those in the unspiked wastes.

Because of budgetary considerations, a spiking scheme was used to minimize the number of analyses required for each waste. The scheme involved spiking each waste in advance with a number of pairs of chemically compatible compounds. Each pair represents a different compound class as indicated in Table 2. The two compounds of each pair were selected on the basis of similar properties (volatility, solubility, polarity, or acidity) that would lead to similar recovery efficiencies. A study reported in the Phase II report demonstrated that the two compounds in each pair did indeed give comparable recovery efficiencies. One compound from each pair was spiked at a relatively low level and the other at an approximately five-fold higher level. With this approach, data for the determination of unspiked components and data for the recoveries of different classes of compounds at two spike levels were obtained simultaneously with a single GC/MS run.

The high and low levels used corresponded to those levels that would give approximately 50 ng and 250 ng of volatile compounds or 10 ng and 50 ng of semivolatile compounds on the GC column during analysis if 100% recovery were achieved. Since the degree of dilution or concentration required for each waste varied widely from waste-to-waste, the actual spike level used also varied widely from waste-to-waste, as shown in Tables 3 and 4.

Since the spike concentrations were relatively high, it was not possible to spike the wastes with solutions of the spiking compounds without significantly changing the nature of the sample and interfering with the determination of volatile compounds. The volatile compounds were readily miscible with each other and were mixed to give a single neat solution prior to spiking. The neat semivolatile compounds, both liquid and solid materials, were added to a glass mortar and pestle and ground to a thin slurry of finely divided particles prior to spiking. The spiking of each waste was conducted in a manner that resulted in a homogeneous spiked sample which was not subject to phase separation. The details of the spiking and homogenizing procedures were described in the Phase II report.

Design of Collaborative Test

Each participating laboratory was sent detailed descriptions of the two analysis methods, ampoules of the standard solutions, samples of all of the spiked wastes and a sample of a contaminated river sediment, ILS-9, which is NBS Standard Reference Material No. 1645. ILS-9 was included to obtain reference data for future work. Each laboratory was requested to analyze three replicates

TABLE 1. WASTE SAMPLES USED IN THE STUDY

Program Identification Number	Waste Name	Physical Description	Analyses Performed[(a)]
ILS-2	Spiked latex paint waste	Semi-solid	s,v
ILS-3	Spiked ethanes spent catalyst	Oily powder	s,v
ILS-4	Spiked coal gasification tar	Tar	s,v
ILS-5	Spiked oxychlorination spent catalyst	Pelletized solid	s,v
ILS-6	Spiked POTW sludge	Wet filter cake	s,v
ILS-7	Spiked herbicide acetone-water	Liquid	v
ILS-8	Spiked chlorinated ethanes waste	Liquid	v
ILS-9	Contaminated river sediment	Oily powder	s

[(a)] S = determination of semivolatile compounds
V = determination of volatile compounds

of each sample to determine volatile compounds and three replicates to determine semivolatile compounds as indicated In Table 1. The laboratories were requested to search for 53 specific volatile compounds and 140 specific semivolatile compounds and quantify the amounts of any compounds found. The specific compounds are listed in Table 5. These compounds were selected as representative of various classes of compounds and to challenge the method and its applicability.

The laboratories were also requested to report retention times or relative retention times found, response factors used, and to quantify up to 10 major unlisted compounds found in each sample. The detailed instructions sent to each laboratory are given in Appendix E. The laboratories were sent special report forms for reporting all data requested. Copies of the forms for reporting data from the determination of volatile and semivolatile compounds are given in Appendix F and Appendix G, respectively.

Data Processing Procedures

The data reported by the participating laboratories of this collaborative study include the amount of compound found in the sample (AF), the response factor (RF) and the retention time (RT) or relative retention times (RRT). These data were reported by nine laboratories for 53 volatile compounds in each of seven sample types, and for 140 semivolatile compounds in each of six sample types. Data on the amount-found AF have been summarized in terms of percent of compound recovered, percent of data recovered and within and between laboratory relative precision.

Since each of the nine laboratories were required to make three replicate analyses, there were potentially 27 values to be reported, for each compound, in each sample type. However, due to various causes, data were not always reported for each replication.

TABLE 2. SPIKING COMPOUNDS

Volatile Compounds

Low-boiling Halocarbons

1,1,1-Trichloroethane
1,2-Dichloropropane

High-boiling Halocarbons

Bromoform
1,1,2,2-Tetrachloroethane

Aromatic Hydrocarbons

Ethylbenzene
Chlorobenzene

Ketone

2-Hexanone

Nitriles

Propionitrile
2-Chloroacrylonitrile

Semivolatile Compounds

Aliphatic Halocarbon

Hexachloroethane

Low-boiling Aromatic Halocarbons

4-Chlorotoluene
1,4-Dichlorobenzene

High-boiling Aromatic Halocarbons

Pentachlorobenzene
Hexachlorobenzene

Chlorinated Pesticides

p,p'-DDD
p,p'-DDT

Low-boiling PAHs

2-Ethylnaphthalene
1-Chloronaphthalene

Chloroanilines

4-Chloroaniline
4-Chloro-2-methylaniline

Nitroanilines

3-Nitroaniline
2-Chloro-4-nitroaniline

Pyridines

2,4,6-Trimethylpyridine
4-t-Butylpyridine

Quinolines

Quinoline
4-Methylquinoline

Haloethers

Bis(2-chloroethyl)ether
Bis(2-chloroethoxy)ethane

(contained)

TABLE 2. (Continued)

Semivolatile Compounds

Mid-boiling PAHs

Fluoranthene
Pyrene

Carbazole

1,2,7,8-Dibenzocarbazole

Aromatic Nitro Cpds.

1,3-Dinitrobenzene
2,6-Dinitrotoluene

Low-acidity Phenols

2-Chlorophenol
2,6-Dimethylphenol

High-acidity Phenols

4-Nitrophenol
2,4-Dinitrophenol

Phosphates

Triphenyl phosphate
Tri-p-tolyl phosphate

Quinones

Anthraquinone
2-Methylanthraquinone

Aromatic Ketones

Acetophenone
Propiophenone

Benzoic Acids

4-Chlorobenzoic acid
4-Bromobenzoic acid

The percent of compound recovered was calculated by

$$\% \text{ Recovery} = \frac{\sum_{i,j} AF_{ij}}{IAF + SLQ} \times 100 \qquad (1)$$

where IAF is the initial amount found in the sample by Battelle analysis, and SLQ is the spike level quantity. The summation is taken over all AF data reported. The percent of AF data reported was calculated by dividing the number of data reported by 27, the maximum number of available data points.

For each combination of sample type and compound, the data were analyzed using the random components analysis of variance model

$$AF_{ij} = \mu + L_i + \epsilon_{ij} \qquad \begin{array}{l} i = 1,2,\ldots, 9 \\ j = 1,2,3 \end{array} \qquad (2)$$

TABLE 3. CONCENTRATION OF VOLATILE COMPOUNDS SPIKED INTO WASTE SAMPLES

Compound Number	Compound	Spike Concentration, µg/g						
		ILS-2 Latex	ILS-3 EtCat	ILS-4 Coal Tar	ILS-5 Oxycat	ILS-6 POTW	ILS-7 Herb Acet	ILS-8 Cl Et Waste
12	Propionitrile	200	500	500	25	5	600	16000
24	2-Chloroacrylonitrile	1000	2000	100	5	30	100	4000
25	1,1,1-Trichloroethane	800	500	100	5	25	100	24000
33	1,2-Dichloropropane	200	3000	400	20	5	500	4000
44	Bromoform	1000	2000	100	5	30	100	4000
46	2-Hexanone	800	500	100	5	25	100	24000
47	1,1,2,2-Tetrachloroethane	200	500	500	25	5	600	16000
50	Chlorobenzene	200	500	600	30	20	100	20000
51	Ethylbenzene	1200	2500	100	5	5	400	4000

TABLE 4. CONCENTRATION OF SEMIVOLATILE COMPOUNDS SPIKED INTO WASTE SAMPLES

		Spike Concentration, µg/g				
Compound Number	Compound	ILS-2 Latex	ILS-3 EtCat	ILS-4 Coal Tar	ILS-5 Oxycat	ILS-6 POTW
5	4-Chlorotoluene	600	800	1900	4	20
12	Bis(2-chloroethyl)ether	500	200	11000	24	20
13	2-Chlorophenol	600	800	1100	4	20
15	2,4,6-Trimethylpyridine	600	800	1900	4	20
16	1,4-Dichlorobenzene	100	200	7600	16	100
22	Acetophenone	100	1000	1900	4	20
25	Hexachloroethane	500	200	11400	24	20
28	4-t-Butylpyridine	100	200	7600	16	100
33	2,4-Dimethylphenol	100	200	7600	16	100
36	Propiophenone	400	200	9500	20	120
43	4-Chloroaniline	600	800	1900	4	20
45	Hexachloropropene	100	1200	1900	4	80
50	Quinoline	500	200	11400	24	20
51	Bis(2-chloroethoxy)ethane	100	1200	1900	4	80
56	4-Chloro-3-methylaniline	100	200	7600	16	100
57	4-Chlorobenzoic acid	500	200	11400	24	20
64	1-Chloronaphthalene	100	1200	1900	4	80
65	4-Methylquinoline	100	1200	1900	4	80
66	2-Ethylnaphthalene	500	200	11400	24	20
69	4-Bromobenzoic acid	100	1200	1900	4	80
74	1,3-Dinitrobenzene	500	200	11400	24	20
76	2,6-Dinitrotoluene	100	1200	1900	4	80
77	3-Nitroaniline	500	200	11400	24	20
80	2,4-Dinitrophenol	400	200	9500	20	120
84	4-Nitrophenol	100	1000	1900	4	20
85	Pentachlorobenzene	100	200	9600	16	100
98	2-Chloro-4-nitroaniline	100	1200	1900	4	80
100	Hexachlorobenzene	600	800	1900	4	20
117	Anthraquinone	600	800	1900	4	20
118	Fluoranthene	100	1000	1900	4	20
120	2-Methylanthraquinone	100	200	7600	16	100
121	Pyrene	400	200	7500	20	120
123	4,4'-DDD	100	1000	1900	4	20
125	4,4'-DDT	400	200	9500	20	120
126	Triphenyl phosphate	600	800	1900	4	20
132	Tri-(p-toly)phosphate	100	200	7600	16	100
137	Dibenzocarbazole	100	1200	1900	4	80

TABLE 5. SPECIFIC COMPOUNDS SEARCHED FOR IN SAMPLES

VOLATILES

Purgeable Halocarbons

Chloromethane
Bromomethane
Vinyl chloride
Chloroethane
Methylene chloride
Trichlorofluoromethane
1,1-Dichloroethene
1,1-Dichloroethane
trans-1,2-Dichloroethane
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Carbon tetrachloride
Bromodichloromethane
1,2-Dichloropropane
trans-1,3-Dichloropropene
Trichloroethene
Dibromochloromethane
1,1,2-Trichloroethane
cis-1,3-Dichloropropene
2-Chloroethylvinyl ether
Bromoform
1,1,2,2-Tetrachloroethane
Tetrachloroethane
Chlorobenzene
1,1,2-Trichlorotrifluoroethane
Dibromoethane
Allyl chloride
Ethylene dibromide
2-Chloropropane
1-Chlorobutane

Purgeable Hydrocarbons

Benzene
Toluene
Ethylbenzene
o-Xylene
Styrene

Purgeable Oxygen, Sulfur, or Nitrogen Compounds

2-Butanone
4-Methyl-2-pentanone
2-Hexanone
Carbon disulfide
Dimethyl disulfide
Acrylonitrile
2-Chloroacrylonitrile
Acetonitrile
Dichloroacetonitrile
n-Propionitrile
Acrolein
Vinyl acetate
Dimethyl sulfide
Diethyl ether
Acetone
Methyl acrylate
Methyl methacrylate

SEMIVOLATILES

Aliphatic Halocarbons

1,4-Dichlorobutane
Pentachloroethane
Hexachloroethene
Hexachloropropene
Hexachlorobutadiene

Aromatic Halocarbons

4-Chlorotoluene
Bromobenzene
1,2-Dichlorobenzene
1,4-Dichlorobenzene
1,2,4-Trichlorobenzene
1,2,4,5-Tetrachlorobenzene
Pentachlorobenzene

(continued)

TABLE 5. (Continued)

SEMIVOLATILES (continued)

Aromatic Halocarbons (continued)

Hexachlorobenzene
3,3'-Dichlorobiphenyl
4,4'-Dichlorobiphenyl
2,2',4,4'-Tetrachlorobiphenyl
Benzal Chloride
2,2',4,4',6,6'-Hexachlorobiphenyl
Benzyl chloride
1-Chloronaphthalene
2-Chloronaphthalene
α,α,α-Trichlorotoluene

Aromatic Hydrocarbons

Naphthalene
1,2,4-Trimethylbenzene
1,2,4,5-Tetramethylbenzene
Biphenyl
Acenaphthylene
Acenaphthene
2-Methylnaphthalene
2-Ethylnaphthalene
2,3-Dimethylnaphthalene
1,2,3,4-Tetrahydronaphthalene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene

Amines

Aniline
4-Chloroaniline
4-Bromoaniline
2-Nitroaniline

Aromatic Nitro Compounds

Nitrobenzene
1,3-Dinitrobenzene
2-Nitrotoluene
4-Nitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1-Chloro-4-nitrobenzene
2,4-Dinitrochlorobenzene

Phenols

2-Chlorophenol
2-Nitrophennol
Phenol
2,4-Dimethylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
4-Chloro-3-methylphenol
2-Methylphenol
4-Methylphenol
Thiophenol
4-Chlorophenol
2,6-Dichlorophenol
2,4,5-Trichlorophenol
Hexachlorophene
4-Hydroxybiphenyl
2-Naphthol
4-t-Butylphenol
2-Chloro-4-nitrophenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
Pentachlorophenol
4-Nitrophenol
2,6-Di-t-butyl-4-methylphenol
2,4-Di-t-butylphenol
Diethylstilbestrol

Chlorinated Pesticides

4,4'-DDD
4,4'-DDE
4,4'-DDT

(continued)

TABLE 5. (Continued)

SEMIVOLATILES (continued)

Amines (continued)

3,4-Dichloroaniline
2,4,5-Trichloroaniline
3-Nitroaniline
4-Chloro-2-nitroaniline
2,4-Dinitroaniline
N-Methylaniline
4-Chloro-o-toluidine
4-Methylaniline
2,6-Dimethylaniline
4-Aminobiphenyl
1-Aminonaphthalene
N,N-Dimethylaniline
Pyridine
4-Methylpyridine
2,4-Dimethylpyridine
4-t-Butylpyridine
1,2,7,8-Dibenzocarbazole
2,4,6-Trimethylpyridine
Quinoline
4-Methylquinoline
Acridine
Carbazole
3,3'-Dichlorobenzidine
Diphenylamine

Ketones

Anthraquinone
2-Methylanthraquinone
Propiophenone
Acetophenone

Haloethers

Bis(2-chloroethyl) ether
Bis(2-chloroethoxy)ethane
4-Chlorophenyl phenyl ether

Chlorinated Pesticides (continued)

Methoxychlor
Trifluralin
Pentachloronitrobenzene

Phthalates

Dimethyl phthalate
Di-n-butyl phthalate
Di(2-ethylhexyl) phthalate

Phosphates

Tri(p-tolyl) phosphate
Triphenyl phosphate

Aldehydes

Benzaldehyde
4-Chlorobenzaldehyde

Esters and Sulfides

Anisole
Phenyl ether
Dibenzofuran

Acids

4-Chlorobenzoic acid
Benzoic acid
4-Bromobenzoic acid
2,4-Dichlorophenoxyacetic acid
2,4,5-Dichlorophenoxyacetic acid

Miscellaneous

Azobenzene
Acetanilide
Benzyl alcohol
Di(2-ethylhexyl) sebacate

where AF_{ij} was the amount of compound found on the j^{th} replication by the i^{th} laboratory. L_i was the random systematic error due to laboratory i and ε_{ij} was the random within-laboratory error. It was assumed that L_i was distributed normally with mean zero and variance σ_L^2. The within-laboratory error term, ε_{ij}, was assumed to be normally distributed with mean zero and variance σ_ε^2. The total variance for the AF data was given by

$$\sigma_T^2 = \sigma_L^2 + \sigma_\varepsilon^2. \qquad (3)$$

Applying this model and analysis of variance techniques, the total, between-laboratory and within-laboratory relative standard deviations defined by $\sigma_T/\mu \times 100$, $\sigma_L/\mu \times 100$, and $\sigma\varepsilon/\mu \times 100$, respectively, were estimated using the AF data obtained from the laboratories. Since there were instances of missing data, appropriate formulas for the construction of one-way analysis of variance tables with unequal samples sizes were employed (4, 5).

In addition to the above analyses, the percent recovery of each compound and sample type was calculated for each laboratory as

$$\%\ \text{Recovery} = \frac{\sum_j AF_{ij}}{IAF + SLQ} \times 100 \qquad (4)$$

RESULTS AND DISCUSSION

The participating laboratories were required to report the retention times and response factors for the semivolatile and volatile compounds found in each waste sample. A summary of these data with variability expressed as percent relative standard deviation (RSD) is provided in Tables 6 and 7. The percent RSD for the relative retention times of semivolatile compounds was generally less than five percent and ranged from 15 to 30 percent for the volatile compounds. The response factor data generated by this program represent the largest reported volume of comparative data for this parameter. The response factors RSDs for the semivolatile compounds were generally less than 40 percent and the volatile compound RSDs ranged from 15 to 80 percent.

The average percent recoveries and the total, between laboratory, and within laboratory relative standard deviations for the spiked volatile compounds in the seven wastes analyzed to determine volatile components are given in Tables 8 to 14. These data tables include the amount of compound spiked and amount-found (µg/g) for each of the reported spiked compounds and the amount-found for listed nonspiked compounds reported by a significant number of laboratories. The amount of data reported by the nine participants is also provided. If data were reported for fewer than 20 percent of the analytical runs the percent RSDs were not determined. The variability of volatile organic analysis (VOA) results exhibited a dependence on sample matrix. For example, the average of the average percent recovery and range for four samples are summarized in Table 15. Variability of data reported by the laboratories was evident and was not reproducible on a per sample basis, i.e., a certain laboratory could report a larger volume of data for one sample than the other laboratories and report the fewest number for another sample. For example, for ILS-2 the number of compounds reported ranged from 6 to 9 with an average of 8.

The within laboratory variability for analysis of volatiles was generally less than 30 percent but ranged from 5 to 300 percent depending on compound. The total variability generally ranged from 20 to 80 percent for most of the waste samples. The between-laboratory variability was usually less than 70 percent but ranged from 5 to 300 percent. The higher variabilities, both total and component, were reported for non-spiked compounds such as methylene chloride, dichloroethane, chloromethane, and chloroform. Only in the case of sample ILS-4 were high percent RSDs reported for spiked compounds.

The corresponding summary data for the spiked semivolatile compounds in the six wastes analyzed to determine semivolatile components are given in Tables 16 to 21. The sample-to-sample variability noted for the volatile compounds was also evident for the semivolatile compound analyses. Summary data for three samples are presented in Table 22. The differences in amount of data reported were more remarkable for the semivolatile determinations than for the

TABLE 6. VARIABLITY OF RELATIVE RETENTION TIMES AND RESPONSE FACTORS FOR THE DETERMINATION OF SEMIVOLATILE COMPOUNDS

Cpd. No.	Compound	Internal Standard	Relative Retention Time(a)	% RSD(b) of Relative Retention Time	Response Factor(c)	% RSD(b) of Response Factor
6.	4-Chlorotoluene	D_5-Bromobenzene	1.084	2.7	0.62	26
12.	Bis(2-chloroethyl)ether	D_5-Bromobenzene	1.173	5.0	1.31	20
13.	2-Chlorophenol	D_5-Bromobenzene	1.177	5.0	1.05	25
15.	2,4,6-Trimethylpyridine	D_5-Bromobenzene	1.237	7.4	0.83	67
16.	1,4-Dichlorobenzene	D_5-Bromobenzene	1.233	6.8	1.47	25
22.	Acetophenone	D_8-Naphthalene	0.838	3.4	0.58	23
25.	Hexachloroethane	D_8-Naphthalene	0.850	2.6	0.19	19
28.	4-t-Butylpyridine	D_8-Naphthalene	0.892	1.5	0.48	28
33.	2,4-Dimethylphenol	D_8-Naphthalene	0.951	1.1	0.37	29
36.	Propiophenone	D_8-Naphthalene	0.978	0.4	0.89	25
43.	4-Chloroaniline	D_8-Naphthalene	1.030	0.8	0.34	51
50.	Quinoline	D_8-Naphthalene	1.077	1.1	0.82	11
51.	Bis(2-chloroethoxy)ethane	D_8-Naphthalene	1.128	2.4	0.42	38
56.	4-Chloro-2-methylaniline	D_{10}-Acenaphthene	0.845	2.4	0.82	88
57.	4-Chlorobenzoic acid	D_{10}-Acenaphthene	0.877	3.5	0.10	27
64.	4-Chloronaphthalene	D_{10}-Acenaphthene	0.918	1.4	1.27	29
65.	4-Methylquinoline	D_{10}-Acenaphthene	0.919	1.1	0.92	39
66.	2-Ethylnaphthalene	D_{10}-Acenaphthene	0.939	3.3	1.28	29
69.	4-Bromobenzoic acid	D_{10}-Acenaphthene	0.967	2.2	0.04	34
74.	1,3-Dinitrobenzene	D_{10}-Acenaphthene	0.973	0.4	0.25	22
76.	2,6-Dinitrotoluene	D_{10}-Acenaphthene	0.983	0.3	0.29	16
77.	3-Nitroaniline	D_{10}-Acenaphthene	1.005	0.7	0.19	62
84.	4-Nitrophenol	D_{10}-Acenaphthene	1.031	1.1	0.31	112
85.	Pentachlorobenzene	D_{10}-Acenaphthene	1.033	0.4	0.49	27

(continued)

TABLE 6. (Continued)

Cpd. No.	Compound	Internal Standard	Relative Retention Time[a]	% RSD[b] of Relative Retention Time	Response Factor[c]	% RSD[b] of Response Factor
98.	2-Chloro-4-nitroaniline	D_{10}-Phenanthrene	0.953	0.3	0.12	11
100.	Hexachlorobenzene	D_{10}-Phenanthrene	0.963	0.3	0.26	26
117.	Anthraquinone	D_{10}-Pyrene	0.940	0.6	0.30	11
118.	Fluoranthene	D_{10}-Pyrene	0.979	0.2	0.94	32
120.	2-Methylanthraquinone	D_{10}-Pyrene	0.997	0.1	0.24	21
121.	Pyrene	D_{10}-Pyrene	1.001	0.1	0.94	33
123.	4,4'-DDD	D_{12}-Chrysene	0.934	0.4	0.61	47
125.	4,4'-DDT	D_{12}-Chrysene	0.962	0.2	0.42	52
126.	Triphenyl phosphate	D_{12}-Chrysene	0.976	0.2	0.21	39
132.	Tri-(p-tolyl)phosphate	D_{12}-Benzo(a)pyrene	0.955	1.3	0.21	37
137.	Dibenzocarbazole	D_{12}-Benzo(a)pyrene	1.106	4.9	0.42	34

(a) Average of all of the relative retention times, relative to the internal standard, reported by the participating laboratories for the determination of the compound in ILS-2.

(b) Percent relative standard deviation.

(c) Average of all of the response factors, relative to the internal standard, reported by the participating laboratories for the determination of the compound in ILS-2.

TABLE 7. VARIABILITY OF RETENTION TIMES AND RESPONSE FACTORS FOR THE DETERMINATION OF VOLATILE COMPOUNDS

Cpd. No.	Compound	Retention Time[(a)] sec	% RSD[(b)] of Retention Time	Response Factor[(c)]	% RSD[(b)] of Response Factor
12.	Propionitrile	551	32	0.15(DCE)	74
24.	2-Chloroacrylonitrile	760	22	2.31(DCE)	67
25.	1,1,1-Trichloroethane	787	20	6.90(DCE)	75
33.	1,2-Dichloropropane	952	19	0.30(Bz)	33
44.	Bromoform	1170	17	0.24(Bz)	80
46.	2-Hexanone	1309	15	0.06(EBz)	71
47.	1,1,2,2-Tetrachloroethane	1308	14	0.27(EBz)	47
50.	Chlorobenzene	1472	13	0.58(EBz)	15
51.	Ethylbenzene	1618	14	0.88(EBz)	20

(a) Average of all of the retention times reported by the participating laboratories for the determination of the compound in ILS-8.

(b) Percent relative standard deviation.

(c) Average of all of the response factors, relative to the internal standard given in parentheses, reported by the participating laboratories for the determination of the compound in ILS-8. DCe=D_4-1,2-dichlo ethane; Bz=D_6-benzene; and EBz=D_5-ethylbenzene.

TABLE 8. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-2

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(d)
12.	Propionitrile	200	(b)	(b)	(b)	(b)	(b)	11
24.	2-Chloroacrylonitrile	1000	431	43	34	28	20	100
25.	1,1,1-Trichloroethane	800	728	91	31	23	20	100
33.	1,2-Dichloropropane	200	190	95	25	18	17	100
44.	Bromoform	1000	1170	117	77	69	34	100
46.	2-Hexanone	800	680	85	31	25	19	89
47.	1,1,2,2-Tetrachloroethane	200	179	90	34	26	22	89
50.	Chlorobenzene	200	202	101	23	17	16	96
51.	Ethylbenzene	1200	1740	145	19	6	18	100
36.	Trichloroethylene	0	25	(c)	93	88	30	56
48.	Tetrachloroethylene	0	158	(c)	72	69	22	100
53.	o-Xylene	0	1130	(c)	76	73	19	89

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 9. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-3

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found Total	Between Lab. Component	Within Lab. Component	Percent of Amount-Found Data Reported(d)
12.	Propionitrile	500	(b)	(b)	(b)	(b)	(b)	0
24.	2-Chloroacrylonitrile	2000	1570	78	104	30	100	96
25.	1,1,1-Trichloroethane	500	5730	1150	67	54	39	93
33.	1,2-Dichloropropane	3000	2090	70	48	42	23	96
44.	Bromoform	2000	1340	67	51	39	33	85
46.	2-Hexanone	500	353	71	56	31	47	52
47.	1,1,2,2-Tetrachloroethane	500	450	90	40	27	29	93
50.	Chlorobenzene	500	511	102	49	45	19	96
51.	Ethylbenzene	2500	1660	67	38	33	19	96
1.	Chloromethane	0	486	(c)	161	154	47	63
16.	trans,1,2-Dichloroethylene	0	870	(c)	70	69	14	74
17.	1,1-Dichloroethane	0	3940	(c)	70	65	27	96
19.	Chloroform	0	260	(c)	70	65	25	74

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 10. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-4

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
12.	Propionitrile	500	1110	223(e)	133	127	41	22
24.	2-Chloroacrylonitrile	100	(b)	(b)	(b)	(b)	(b)	4
25.	1,1,1-Trichloroethane	100	73	73	86	72	47	78
33.	1,2-Dichloropropane	400	304	76	33	27	19	100
44.	Bromoform	100	742	742(e)	204	204	16	56
46.	2-Hexanone	100	825	825(e)	178	171	49	37
47.	1,1,2,2-Tetrachloroethane	500	385	77	68	64	22	67
50.	Chlorobenzene	600	492	82	73	66	32	100
51.	Ethylbenzene	100	90	90(c)	63	52	35	89
19.	Chloroform	0	141	(c)	317	64	310	100
36.	Trichloroethylene	0	168	(c)	187	187	12	52
40.	Dibromoethanethane	0	46	(c)	39	23	32	63
48.	Tetrachloroethylene	0	2630	(c)	143	137	42	100
49.	Toluene	0	95	(c)	87	79	34	89
52.	Styrene	0	113	(c)	65	60	27	78
53.	o-Xylene	0	111	(c)	70	60	37	78

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).

The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 11. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-5

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(d)
12.	Propionitrile	25	(b)	(b)	(b)	(b)	(b)	11
24.	2-Chloroacrylonitrile	5	(b)	(b)	(b)	(b)	(b)	11
25.	1,1,1-Trichloroethane	5	(b)	(b)	(b)	(b)	(b)	11
33.	1,2-Dichloropropane	20	4	18	53	51	17	56
44.	Bromoform	5	3	48	77	75	17	67
46.	2-Hexanone	5	(b)	(b)	(b)	(b)	(b)	11
47.	1,1,2,2-Tetrachloroethane	25	13	51	51	47	18	100
50.	Chlorobenzene	30	10	34	63	63	7	89
51.	Ethylbenzene	5	3	52	30	29	4	41
5.	Methylene chloride	0	124	(c)	266	189	187	78
19.	Chloroform	0	4	(c)	219	88	200	56

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 12. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-6

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(d)
12.	Propionitrile	5	(b)	(b)	(b)	(b)	(b)	0
24.	2-Chloroacrylonitrile	30	(b)	(b)	(b)	(b)	(b)	4
25.	1,1,1-Trichloroethane	25	(b)	(b)	(b)	(b)	(b)	7
33.	1,2-Dichloropropane	5	1	26	22	21	8	48
44.	Bromoform	30	(b)	(b)	(b)	(b)	(b)	4
46.	2-Hexanone	25	11	44	124	109	59	26
47.	1,1,2,2-Tetrachloroethane	5	(b)	(b)	(b)	(b)	(b)	4
50.	Chlorobenzene	20	11	56	47	44	18	100
51.	Ethylbenzene	5	4	76	35	15	32	89
5.	Methylene chloride	0	27	(c)	307	19	307	63
17.	1,1-Dichloroethane	0	1	(c)	59	56	17	52
38.	1,1,2-Trichloroethane	0	5	(c)	34	25	23	78
48.	Tetrachloroethylene	0	2	(c)	27	26	8	67
53.	o-Xylene	0	2	(c)	75	55	52	67

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 13. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-7

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(d)
12.	Propionitrile	600	(b)	(b)	(b)	(b)	(b)	11
24.	2-Chloroacrylonitrile	100	(b)	(b)	(b)	(b)	(b)	4
25.	1,1,1-Trichloroethane	100	28	28	68	65	20	78
33.	1,2-Dichloropropane	500	250	50	38	37	9	100
44.	Bromoform	100	30	30	96	92	24	56
46.	2-Hexanone	100	102	102	119	71	95	52
47.	1,1,2,2-Tetrachloroethane	600	212	35	44	36	26	100
50.	Chlorobenzene	100	49	49	45	43	12	100
51.	Ethylbenzene	400	230	57	40	38	10	89
6.	Acetone	0	10800	(c)	92	91	13	78
36.	Trichloroethylene	0	87	(c)	56	55	14	100

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 14. RECOVERY VARIABILITY OF VOLATILE COMPOUNDS FROM SAMPLE ILS-8

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
12.	Propionitrile	16000	17000	106	28	27	8	26
24.	2-Chloroacrylonitrile	4000	5020	126	50	48	13	78
25.	1,1,1-Trichloroethane	24000	24300	101	46	43	16	89
33.	1,2-Dichloropropane	4000	2960	74	47	45	16	78
44.	Bromoform	4000	3290	82	60	58	16	89
46.	2-Hexanone	24000	20900	87	53	48	24	89
47.	1,1,2,2-Tetrachloroethane	16000	12300	77	49	48	10	100
50.	Chlorobenzene	20000	18100	91	56	53	18	100
51.	Ethylbenzene	4000	3760	94	61	57	21	89
15.	1,1-Dichloroethane	0	7290	(c)	176	174	28	89
16.	trans-1,2-Dichloroethylene	0	13200	(c)	84	82	19	100
17.	1,1-Dichloroethane	0	3760	(c)	52	49	18	78
19.	Chloroform	0	1770	(c)	49	46	17	100
26.	Carbon tetrachloride	0	520000	(c)	66	63	19	100
36.	Trichloroethylene	0	136000	(c)	65	63	16	100

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 15. SAMPLE-TO-SAMPLE RECOVERY DEPENDENCIES-VOA

Sample	Average Percent Recovery	Range[(a)]
ILS-2	96	40-150
ILS-3	78	67-102
ILS-5	41	18-52
ILS-8	93	74-126

(a) Excludes obvious outliers

volatile determinations. For example, for ILS-3, the number of compounds reported varied from 1 to 27 with 20 being the average number of compounds reported. The total relative standard deviation generally ranged from 30 to 80 percent. The relative standard deviation for the within-laboratory component was less than 30 percent and the between-laboratory variability was about twice that value. The ranges of both components were the same as that reported for volatile results, namely 5 to 300 percent. No difference in range of values was apparent for the spiked versus non-spiked compounds, however, some of the higher recoveries may be attributable to differential extraction efficiencies between analytes and internal standards and to background contaminants such as phthalates.

The results for ILS-9, the National Bureau of Standards SRM, presented in Table 21 were surprisingly variable. The total variabilities ranged from 28 to 338 percent and averaged 160 percent. The quantities of compounds found were relatively lower in many of the samples, however, the quantities of compounds found in ILS-5 and ILS-6 were comparable. The degree of homogeneity of ILS-9 should be better than the other program samples since NBS prepared this sample.

An inspection of the data reported by each individual laboratory revealed that most of the variability could be attributed to outlier values reported by one laboratory. In some cases a significant portion of the variability was also caused by outlier values reported by a second laboratory. The improvement in the total variabilities obtained by omitting the data from one laboratory or two laboratories in the calculation are shown in Table 23. By omitting the data from two laboratories the total variabilities ranged from only 13 to 90 percent and averaged 31 percent. An average total variability of 31 percent was considered excellent. The within-laboratory component of the variability would be much less.

The above treatment could undoubtedly be applied to the data from other samples and provide significant improvements in the precision. A very important next step would be to investigate the supplemental data in detail to determine the causes of other outliers. The information on the probable causes of outliers would be used to modify the method instructions and quality control protocols to reduce the number of outliers generated in any future application of the methods.

TABLE 16. RECOVERY VARIABILITY OF SEMIVOLATILE COMPOUNDS FROM SAMPLE ILS-2

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
6.	4-Chlorotoluene	600	363	61	63	60	17	96
12.	Bis(2-chloroethyl)ether	500	310	62	62	60	17	100
13.	2-Chlorophenol	600	358	60	52	47	21	100
15.	2,4,6-Trimethylpyridine	600	692	115	91	87	25	59
16.	1,4-Dichlorobenzene	100	36	36	63	62	12	70
22.	Acetophenone	100	103	103	47	41	23	89
25.	Hexachloroethane	500	257	51	55	29	47	89
28.	4-t-Butylpyridine	100	47	47	53	48	22	44
33.	2,4-Dimethylphenol	100	71	71	34	20	28	56
36.	Propiophenone	400	254	64	46	41	20	89
43.	4-Chloroaniline	600	337	56	257	134	219	74
50.	Quinoline	500	313	63	38	27	27	100
51.	Bis(2-chloroethoxy) ethane	100	62	62	(b)	(b)	(b)	56
56.	4-Chloro-2-methylaniline	100	61	61	73	66	33	41
57.	4-Chlorobenzoic acid	500	393	79	(b)	(b)	(b)	33
64.	1-Chloronaphthalene	100	63	63	51	47	20	33
65.	4-Methylquinoline	100	88	88	76	67	35	63
66.	2-Ethylnaphthalene	500	373	74	51	41	30	100
69.	4-Bromobenzoic acid	100	52	52	67	64	19	22
74.	1,3-Dinitrobenzene	500	199	40	49	44	22	63
76.	2,6-Dinitrotoluene	100	64	64	37	32	18	44
77.	3-Nitroaniline	500	406	81	50	44	25	44
80.	2,4-Dinitrophenol	400	(b)	(b)	(b)	(b)	(b)	0
84.	4-Nitrophenol	100	54	54	(b)	(b)	(b)	11
85.	Pentachlorobenzene	100	71	71	43	32	28	74
98.	2-Chloro-4-nitroaniline	100	62	62	42	35	23	22

(continued)

TABLE 16. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
100.	Hexachlorobenzene	600	460	77	43	38	21	100
117.	Anthraquinone	600	403	67	57	49	28	100
118.	Fluoranthene	100	71	71	41	36	20	100
120.	2-Methylanthraquinone	100	71	71	55	49	26	78
121.	Pyrene	400	306	77	40	36	18	100
123.	4,4'-DDD	100	67	67	77	14	75	78
125.	4,4'-DDT	400	225	56	68	37	57	85
126.	Triphenyl phosphate	600	524	87	87	58	65	89
132.	Tri-(p-tolyl) phosphate	100	57	57	64	56	30	63
137.	Dibenzocarbazole	100	109	109	70	58	39	56
29.	1,2,4,5-Tetramethylbenzene	0	25	(c)	69	38	57	63
41.	Naphthalene	0	174	(c)	231	231	14	78
114.	Di-n-butyl phthalate	0	80	(c)	675	165	82	56

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 17. RECOVERY VARIABILITY OF SEMIVOLATILE COMPOUNDS FROM SAMPLE ILS-3

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found Total	Between Lab. Component	Within Lab. Component	Percent of Amount-Found Data Reported(d)
6.	4-Chlorotoluene	800	877	110	96	80	54	89
12.	Bis(2-chloroethyl)ether	200	166	83	49	48	6	67
13.	2-Chlorophenol	800	158	20	27	19	20	67
15.	2,4,6-Trimethylpyridine	800	2460	307	136	131	36	78
16.	1,4-Dichlorobenzene	200	169	84	103	86	57	89
22.	Acetophenone	1000	543	54	88	51	71	89
25.	Hexachloroethane	200	243	122	160	159	17	85
28.	4-t-Butylpyridine	200	92	46	44	37	23	56
33.	2,4-Dimethylphenol	200	(b)	(b)	(b)	(b)	(b)	4
36.	Propiophenone	200	181	90	185	143	117	78
43.	4-Chloroaniline	800	(b)	(b)	(b)	(b)	(b)	11
50.	Quinoline	200	281	141	169	137	99	78
51.	Bis(2-chloroethoxy) ethane	1200	1230	103	138	103	91	100
56.	4-Chloro-2-methylaniline	200	86	43	83	83	10	22
57.	4-Chlorobenzoic acid	200	(b)	(b)	(b)	(b)	(b)	0
64.	1-Chloronaphthalene	1200	(b)	(b)	(b)	(b)	(b)	0
65.	4-Methylquinoline	1200	1790	149	134	104	85	67
66.	2-Ethylnaphthalene	200	(b)	(b)	(b)	(b)	(b)	11
69.	4-Bromobenzoic acid	1200	(b)	(b)	(b)	(b)	(b)	11
74.	1,3-Dinitrobenzene	200	652	326	111	111	7	19
76.	2,6-Dinitrotoluene	1200	1670	139	152	109	105	56
77.	3-Nitroaniline	200	(b)	(b)	(b)	(b)	(b)	7
80.	2,4-Dinitrophenol	200	(b)	(b)	(b)	(b)	(b)	0
84.	4-Nitrophenol	1000	(b)	(b)	(b)	(b)	(b)	11
85.	Pentachlorobenzene	200	279	71	114	91	68	78
98.	2-Chloro-4-nitroaniline	1200	467	39	227	226	13	15

(continued)

TABLE 17. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
100.	Hexachlorobenzene	800	1170	146	123	103	68	89
117.	Anthraquinone	800	1240	155	128	109	67	78
118.	Fluoranthene	1000	907	90	92	75	55	89
120.	2-Methylanthraquinone	200	352	176	100	87	49	67
121.	Pyrene	200	229	115	188	96	162	22
123.	4,4'-DDD	1000	1550	155	118	97	69	89
125.	4,4'-DDT	200	508	254	211	211	13	74
126.	Triphenyl phosphate	800	1180	147	137	110	81	89
132.	Tri-(p-tolyl) phosphate	200	339	170	126	107	67	41
137.	Dibenzocarbazole	1200	263	22	100	78	62	11

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 18. RECOVERY VARIABILITY OF SEMIVOLATILE COMPOUNDS FROM SAMPLE ILS-4

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(d)
6.	4-Chlorotoluene	1900	1490	78	65	50	41	89
12.	Bis(2-chloroethyl)ether	11400	8500	75	86	84	20	96
13.	2-Chlorophenol	1900	2310	122	120	115	32	89
15.	2,4,6-Trimethylpyridine	1900	2270	119	29	23	18	37
16.	1,4-Dichlorobenzene	7600	4950	65	47	42	22	100
22.	Acetophenone	1900	1880	99	82	78	25	89
25.	Hexachloroethane	11400	8980	79	91	86	30	100
28.	4-t-Butylpyridine	7600	6790	89	61	57	23	89
33.	2,4-Dimethylphenol	7600	8840	104	83	80	23	89
36.	Propiophenone	9500	9610	101	74	73	17	89
43.	4-Chloroaniline	1900	2420	127	63	60	17	56
50.	Quinoline	11400	2680	24	72	68	23	89
51.	Bis(2-chloroethoxy) ethane	1900	1870	98	86	81	30	89
56.	4-Chloro-2-methylaniline	7600	6920	91	60	54	24	78
57.	4-Chlorobenzoic acid	11400	15900	139	154	139	67	78
64.	1-Chloronaphthalene	1900	1260	66	32	27	17	44
65.	4-Methylquinoline	1900	2430	128	91	86	30	89
66.	2-Ethylnaphthalene	11400	1410	12	100	95	32	89
69.	4-Bromobenzoic acid	1900	1210	64	40	34	22	22
74.	1,3-Dinitrobenzene	11400	12900	113	105	103	18	78
76.	2,6-Dinitrotoluene	1900	2280	120	105	103	21	78
77.	3-Nitroaniline	11400	14200	125	95	93	23	78
80.	2,4-Dinitrophenol	9500	2010	21	93	89	27	56
84.	4-Nitrophenol	1900	(b)	(b)	(b)	(b)	(b)	11
85.	Pentachlorobenzene	7600	7090	93	74	72	19	100
98.	2-Chloro-4-nitroaniline	1900	2400	127	125	121	29	59

(continued)

TABLE 18. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
100.	Hexachlorobenzene	1900	2060	108	87	82	28	89
117.	Anthraquinone	1900	2180	115	94	91	27	89
118.	Fluoranthene	1900	14400	87(e)	59	39	44	100
120.	2-Methylanthraquinone	7600	8420	111	92	86	32	89
121.	Pyrene	9500	17400	61(f)	54	45	30	100
123.	4,4'-DDD	1900	2120	111	88	81	35	89
125.	4,4'-DDT	9500	9270	98	108	106	22	89
126.	Triphenyl phosphate	1900	2230	117	95	92	24	78
132.	Tri-(p-tolyl) phosphate	7600	10530	139	92	85	35	89
137.	Dibenzocarbazole	1900	(b)	(b)	(b)	(b)	(b)	11
139.	Dibenzo(a,h)anthracene	0	880	(c)	82	45	69	67
11.	Phenol	0	3810	(c)	78	59	51	89
14.	1,2,4-Trimethylbenzene	0	370	(c)	58	52	27	67
20.	2-Methylphenol	0	1040	(c)	78	77	11	74
23.	4-Methylphenol	0	3220	(c)	79	70	37	89
41.	Naphthalene	0	26400	(c)	31	26	17	100
54.	2-Methylanthraquinone	0	16600	(c)	191	189	28	89
63.	Biphenyl	0	1730	(c)	79	76	21	78
72.	Acenaphthylene	0	62000	(c)	98	97	10	89
73.	2,3-Dimethylnaphthalene	0	850	(c)	77	72	27	78
78.	Acenaphthene	0	720	(c)	75	71	22	78
83.	4-Aminobiphenyl	0	5530	(c)	74	72	16	100
90.	4-Chlorophenyl phenyl ether	0	8760	(c)	67	64	19	100

(continued)

TABLE 18. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
107.	Phenanthrene	0	19100	(c)	54	49	23	100
109.	Anthracene	0	6910	(c)	60	53	28	100
110.	Acridine	0	650	(c)	77	74	21	67
111.	Phenanthridine	0	720	(c)	93	91	21	78
112.	Carbazole	0	3520	(c)	87	84	22	89

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

(e) Corrected for the 14,600 µg/g present in the unspiked sample.

(f) Corrected for the 19,000 µg/g present in the unspiked sample.

TABLE 19. RECOVERY VARIABILITY OF SEMIVOLATILE COMPOUNDS FROM SAMPLE ILS-5

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(d)
6.	4-Chlorotoluene	4	(b)	(b)	(b)	(b)	(b)	11
12.	Bis(2-chloroethyl)ether	24	7.2	30	51	50	14	78
13.	2-Chlorophenol	4	(b)	(b)	(b)	(b)	(b)	0
15.	2,4,6-Trimethylpyridine	4	5.3	131	145	118	85	22
16.	1,4-Dichlorobenzene	16	2	8	48	43	22	78
22.	Acetophenone	4	2	26	75	67	32	67
25.	Hexachloroethane	24	2	7	62	54	29	78
28.	4-t-Butylpyridine	16	2	15	87	82	31	67
33.	2,4-Dimethylphenol	16	(b)	(b)	(b)	(b)	(b)	0
36.	Propiophenone	20	9	43	51	48	18	89
43.	4-Chloroaniline	4	(b)	(b)	(b)	(b)	(b)	0
50.	Quinoline	24	7	29	48	38	29	89
51.	Bis(2-chloroethoxy) ethane	4	2	48	68	66	17	56
56.	4-Chloro-2-methylaniline	16	(b)	(b)	(b)	(b)	(b)	0
57.	4-Chlorobenzoic acid	24	7	27	65	49	42	44
64.	1-Chloronaphthalene	4	2	49	43	18	40	44
65.	4-Methylquinoline	4	1	26	125	49	114	67
66.	2-Ethylnaphthalene	24	11	47	47	44	16	89
69.	4-Bromobenzoic acid	4	(b)	(b)	(b)	(b)	(b)	0
74.	1,3-Dinitrobenzene	24	11	46	78	74	25	78
76.	2,6-Dinitrotoluene	4	2	54	68	55	40	52
77.	3-Nitroaniline	24	(b)	(b)	(b)	(b)	(b)	0
80.	2,4-Dinitrophenol	20	2	11	76	71	29	44
84.	4-Nitrophenol	4	(b)	(b)	(b)	(b)	(b)	11
85.	Pentachlorobenzene	16	9	53	53	52	11	78
98.	2-Chloro-4-nitroaniline	4	(b)	(b)	(b)	(b)	(b)	11

(continued)

TABLE 19. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found			Percent of Amount-Found Data Reported(d)
					Total	Between Lab. Component	Within Lab. Component	
100.	Hexachlorobenzene	4	2	50	58	55	18	78
117.	Anthraquinone	4	2	48	80	69	38	81
118.	Fluoranthene	4	3	63	84	55	64	93
120.	2-Methylanthraquinone	16	7	46	64	61	19	78
121.	Pyrene	20	9	44	56	53	19	100
123.	4,4'-DDD	4	3	70	68	60	33	81
125.	4,4'-DDT	20	10	49	76	59	47	89
126.	Triphenyl phosphate	4	2	60	44	39	20	59
132.	Tri-(p-tolyl) phosphate	16	10	59	89	86	23	70
137.	Dibenzocarbazole	4	(b)	(b)	(b)	(b)	(b)	0
39.	2,6-Dichlorophenol	0	1	(c)	48	37	30	56
63.	Biphenyl	0	1	(c)	73	40	61	78
67.	Phenyl ether	0	1	(c)	86	52	69	67
114.	Di-n-butyl phthalate	0	7	(c)	137	122	62	56

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 20. RECOVERY VARIABILITY OF SEMIVOLATILE COMPOUNDS FROM SAMPLE ILS-6

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount-Found Total	Between Lab. Component	Within Lab. Component	Percent of Amount-Found Data Reported(d)
6.	4-Chlorotoluene	20	5	26	97	95	20	33
12.	Bis(2-chloroethyl)ether	20	7	33	55	50	23	22
13.	2-Chlorophenol	20	10	51	46	41	20	44
15.	2,4,6-Trimethylpyridine	20	(b)	(b)	(b)	(b)	(b)	11
16.	1,4-Dichlorobenzene	100	29	29	60	54	26	93
22.	Acetophenone	20	5	24	55	50	24	44
25.	Hexachloroethane	20	(b)	(b)	(b)	(b)	(b)	0
28.	4-t-Butylpyridine	100	45	45	54	50	22	85
33.	2,4-Dimethylphenol	100	50	50	42	39	18	89
36.	Propiophenone	120	25	21	53	46	27	89
43.	4-Chloroaniline	20	(b)	(b)	(b)	(b)	(b)	11
50.	Quinoline	20	5	23	34	23	25	44
51.	Bis(2-chloroethoxy) ethane	80	31	38	43	37	22	78
56.	4-Chloro-2-methylaniline	100	40	40	67	65	19	44
57.	4-Chlorobenzoic acid	20	20	100	110	38	103	22
64.	1-Chloronaphthalene	80	41	52	50	47	17	59
65.	4-Methylquinoline	80	38	48	78	77	13	78
66.	2-Ethylnaphthalene	20	11	56	54	49	23	78
69.	4-Bromobenzoic acid	80	28	35	65	51	41	96
74.	1,3-Dinitrobenzene	20	(b)	(b)	(b)	(b)	(b)	0
76.	2,6-Dinitrotoluene	80	(b)	(b)	(b)	(b)	(b)	0
77.	3-Nitroaniline	20	(b)	(b)	(b)	(b)	(b)	0
80.	2,4-Dinitrophenol	120	(b)	(b)	(b)	(b)	(b)	0
84.	4-Nitrophenol	20	(b)	(b)	(b)	(b)	(b)	0
85.	Pentachlorobenzene	100	52	52	48	42	23	100
98.	2-Chloro-4-nitroaniline	80	(b)	(b)	(b)	(b)	(b)	0

(continued)

TABLE 20. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Recovery(a)	Percent Relative Standard Deviation of Amount Found: Total	Percent Relative Standard Deviation of Amount Found: Between Lab. Component	Percent Relative Standard Deviation of Amount Found: Within Lab. Component	Percent of Amount Found Data Reported(d)
100.	Hexachlorobenzene	20	13	63	46	37	27	44
117.	Anthraquinone	20	7	35	58	55	19	33
118.	Fluoranthene	20	14	59	45	41	18	100
120.	2-Methylanthraquinone	100	36	36	57	51	25	89
121.	Pyrene	120	76	61	52	51	10	100
123.	4,4'-DDD	20	32	162	61	54	27	89
125.	4,4'-DDT	120	(b)	(b)	(b)	(b)	(b)	0
126.	Triphenyl phosphate	20	15	76	99	93	33	33
132.	Tri-(p-tolyl) phosphate	100	68	68	46	41	22	85
137.	Dibenzocarbazole	80	72	89	78	75	18	52
11.	Phenol	0	18	(c)	33	25	21	67
23.	4-Methylphenol	0	29	(c)	40	36	17	81
40.	1,2,4-Trichlorobenzene	0	39	(c)	49	43	25	89
67.	Phenyl ether	0	5	(c)	82	73	37	52
107.	Phenanthrene	0	3	(c)	54	34	42	56
114.	Di-n-butyl phthalate	0	21	(c)	135	94	97	78
131.	Di-(2-ethylhexyl) phthalate	0	30	(c)	75	69	29	100

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) Not determined because amount-found data were reported for fewer than 20 percent of the analytical runs.

(c) Not applicable because the compound was not used as a spike compound.

(d) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).

The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 21. RECOVERY VARIABILITY OF SEMIVOLATILE COMPOUNDS FROM SAMPLE ILS-6

Cpd. No.	Compound	Amount Spiked, µg/g	Amount Found,(a) µg/g	Percent Relative Standard Deviation of Amount-Found: Total	Percent Relative Standard Deviation of Amount-Found: Between Lab. Component	Percent Relative Standard Deviation of Amount-Found: Within Lab. Component	Percent of Amount-Found Data Reported(b)
41.	Naphthalene	0	4	263	125	231	75
72.	Acenaphthylene	0	45	278	87	265	75
78.	Acenaphthene	0	1	28	16	23	63
90.	Fluorene	0	14	305	197	233	59
107.	Phenanthrene	0	28	338	131	311	75
109.	Anthracene	0	10	287	109	265	75
114.	Di-n-butyl phthalate	0	22	218	158	150	63
117.	Anthraquinone	0	15	102	84	59	71
118.	Fluoranthene	0	53	154	65	139	100
121.	Pyrene	0	93	107	50	94	78
127.	Benzo(a)anthracene	0	40	79	41	68	100
130.	Chrysene	0	70	44	29	33	100
134.	Benzo(k)fluoranthene	0	40	127	57	113	88
136.	Benzo(a)pyrene	0	14	95	92	21	88
138.	Indeno(1,2,3 cd)pyrene	0	14	127	78	101	88
139.	Dibenzo(a,h)anthracene	0	10	87	77	40	88
140.	Benzo(g,h,i)perylene	0	18	93	64	67	83

(a) Average of the values reported by the participating laboratories for all analytical runs (maximum of 3 per laboratory) in which the compound was detected and quantified.

(b) The maximum number of analytical runs for which data could be reported in the study was 27 (replicates x 9 labs).
The percent of amount-found data reported =

$$\frac{\text{total number of analytical runs for which data were reported}}{27} \times 100$$

TABLE 22. SAMPLE-TO-SAMPLE RECOVERY DEPENDENCIES-SV

Sample	Average Percent Recovery	Range
ILS-5	68	30-115
ILS-4	95	20-140
ILS-5	44	7-131

The percent recoveries of spiked volatile compounds reported by each laboratory including the total number of spike compounds reported are given in Tables 24 to 30. The corresponding data for the spiked semivolatile compounds are given in Tables 31 to 35. These compilations of data are based on numerical data reported; missing data are not included in the averages as zeros. These data tables were prepared in this format to enable the reader to ascertain specific laboratory results and to facilitate the identification of trends. The total number of spike compounds reported by each laboratory is recorded for purposes of comparison. The individual percent recovery entries for each laboratory may be examined for variability from compound-to-compound, from sample-to-sample, and of course, from laboratory-to-laboratory. These data are particularly useful for identifying anomalous data that may skew the summary statistical data presented in the previous tables. For example, for ILS-3 the data in Table 25 show that all 9 laboratories consistently found larger quantities of 1,1,1-trichloroethane than were spiked. However, only one laboratory, Lab 5, reported excessive quantities of 2-chloroacrylonitrile and 2-hexanone in sample ILS-4 (Table 26). Examination of the raw data shows that abnormally low response factors were used for the quantification; thus, the high average values reported in Table 10 were explained.

The variability in the total number of volatile compounds reported is presented in Table 36 in a matrix for samples versus laboratory. The totals of these columns can be used as a guide to identify difficult samples and to identify overall laboratory performance differences. The two samples for which the poorest results were obtained were ILS-5 (oxychlorination spent catalyst) and ILS-6 (POTW sludge). These two sample matrices would be expected to be the least retentive of volatile compounds and amounts of the components may have been lost during sample storage prior to analysis. Excellent results were obtained with ILS-2, ILS-3 and ILS-8, while ILS-4 and ILS-7 provided intermediate results. The differences in laboratory performance are more difficult to measure in such a complex study. However, the performance of Lab 8 was definitely poorer than the other laboratories for the VOA determinations. The summary data for semivolatile compounds presented in Tables 31-35 are presented in matrix form in Table 37. The poorest performance was experienced by Lab 7 for semivolatiles analyses. An excellent performance may be noted for Lab 2. The problem samples for VOA determinations were also repeated with ILS-5 and ILS-6 being the most difficult. These were closely followed by ILS-3. Excellent results were obtained for ILS-4 (except for Lab 7) and ILS-2. Lab 4 experienced considerable difficulty with ILS-3 while Labs 1 and 5 had unusual detection problems with ILS-5.

TABLE 23. EFFECT OF REMOVING OUTLIERS ON DATA QUALITY FOR THE DETERMINATION OF SEMIVOLATILE COMPOUNDS IN SAMPLE ILS-9

Cpd. No.	Compound	Number of Data Using Given Data Set(a)			Amount Found, µg/g, Using Given Data Set(a)			Percent Relative Standard Deviation Using Given Data Set(a)		
		A	B	C	A	B	C	A	B	C
41.	Naphthalene	18	15	12	4	1	1	263	20	18
72.	Acenaphthylene	18	15	12	45	13	17	278	111	90
18.	Acenaphthene	15	12	9	1	1	1	28	27	24
10.	Fluorene	14	11	8	14	2	1	305	42	23
107.	Phenanthrene	18	15	12	28	3	3	338	26	13
109.	Anthracene	18	15	12	10	2	2	287	87	74
114.	Di-n-butyl phthalate	15	12	9	22	4	5	218	48	30
117.	Anthraquinone	17	14	11	15	10	9	102	30	15
118.	Fluoranthene	24	21	18	53	34	32	154	23	18
121.	Pyrene	24	21	18	93	69	61	107	23	15
127.	Benzo(a)anthracene	24	21	18	40	33	30	79	38	32
130.	Chrysene	24	21	18	70	62	60	44	18	17
134.	Benzo(k)fluoranthene	21	18	15	40	27	26	127	28	28
136.	Benzo(a)pyrene	21	18	15	14	9	8	95	33	18
138.	Indeno(1,2,3 cd)pyrene	21	18	15	14	9	8	127	48	36
139.	Dibenzo(a,h)anthracene	21	18	15	10	7	5	87	73	48
140.	Benzo(g,h,i)perylene	20	17	14	18	13	11	93	48	29

(a) Data set A includes all reported data. The maximum number of data possible is 24 (3 replicates x 8 laboratories). One of the 9 laboratories, with EPA's concurrence, did not analyze ILS-9.
Data set B includes all reported data except that from one laboratory.
Data set C includes all reported data except that from two laboratories.
None of the data reported by Lab 5 was included in sets B and C.

TABLE 24. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-2

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory[a] Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	200	(b)	(b)	(b)	(b)	(b)	(b)	36	(b)	(b)
24.	2-Chloroacrylonitrile	1000	44	66	59	35	38	42	21	38	55
25.	1,1,1-Trichloroethane	800	78	124	112	63	77	78	68	94	124
33.	1,2-Dichloropropane	200	87	137	100	96	78	86	99	66	106
44.	Bromoform	1000	73	134	104	51	328	103	125	60	74
46.	2-Hexanone	800	79	(b)	91	65	137	77	72	94	75
47.	1,1,2,2-Tetrachloroethane	200	86	(b)	95	95	138	85	81	93	45
50.	Chlorobenzene	200	95	80	112	105	97	90	84	95	146
51.	Ethylbenzene	1200	112	168	139	135	148	133	152	154	163
	Total no. of spike compounds reported		8	6	8	8	8	8	9	8	8

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 25. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-3

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	500	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
24.	2-Chloroacrylonitrile	2000	47	195	61	55	50	42	34	112	96
25.	1,1,1-Trichloroethane	500	1285	1137	2448	940	697	940	71	1152	1790
33.	1,2-Dichloropropane	3000	64	78	113	80	32	65	21	79	106
44.	Bromoform	2000	(b)	98	97	35	45	82	54	35	96
46.	2-Hexanone	500	(b)	(b)	(b)	56	120	46	61	(b)	62
47.	1,1,2,2-Tetrachloroethane	500	60	116	134	99	58	74	68	123	81
50.	Chlorobenzene	500	71	123	151	94	35	76	61	117	183
51.	Ethylbenzene	2500	60	67	82	79	31	61	42	110	67
	Total no. of spike compounds reported		6	7	7	8	8	8	8	7	8

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 26. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-4

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory[(a)]								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	500	(b)	(b)	426(c)	(b)	(b)	(b)	20	(b)	(b)
24.	2-Chloroacrylonitrile	100	(b)	(b)	(b)	(b)	295(c)	(b)	(b)	(b)	(b)
25.	1,1,1-Trichloroethane	100	15	161	103	25	18	109	77	(b)	(b)
33.	1,2-Dichloropropane	400	71	93	86	38	55	82	81	64	114
44.	Bromoform	100	(b)	3450(d)	97	19	88	(b)	58	(b)	(b)
46.	2-Hexanone	100	(b)	7	(b)	34	2685(d)	(b)	29	(b)	(b)
47.	1,1,2,2-Tetrachloroethane	500	75	13	84	(b)	159	95	38	(b)	(b)
50.	Chlorobenzene	600	95	8	89	45	71	98	37	89	208
51.	Ethylbenzene	100	127	8	95	53	125	107	46	(b)	161
	Total no. of spike compounds reported		5	7	7	6	8	5	8	2	3

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

(c) Compound was probably misidentified.

(d) Abnormally low response factor was used for the quantification.

TABLE 27. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-5

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	25	(b)	(b)	(b)	(b)	281(c)	(b)	(b)	(b)	(b)
24.	2-Chloroacrylonitrile	5	(b)	42	(b)	(b)	(b)	(b)	(b)	(b)	(b)
25.	1,1,1-Trichloroethane	5	(b)	12	(b)	(b)	(b)	(b)	(b)	(b)	(b)
33.	1,2-Dichloropropane	20	20	21	27	(b)	(b)	23	(b)	2	(b)
44.	Bromoform	5	(b)	94	85	(b)	(b)	43	18	45	2
46.	2-Hexanone	5	(b)	(b)	(b)	(b)	(b)	67	(b)	(b)	(b)
47.	1,1,2,2-Tetrachloroethane	25	52	79	72	20	50	53	44	78	8
50.	Chlorobenzene	30	47	59	52	13	(b)	48	12	41	2
51.	Ethylbenzene	5	47	51	(b)	20	52	69	(b)	(b)	(b)
	Total no. of spike compounds reported		4	7	4	3	3	6	3	4	3

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

(c) Compound was probably misidentified.

TABLE 28. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-6

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	5	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
24.	2-Chloroacrylonitrile	30	(b)	(b)	(b)	(b)	25(c)	(b)	(b)	(b)	(b)
25.	1,1,1-Trichloroethane	25	(b)	1	(b)	(b)	(b)	(b)	(b)	(b)	(b)
33.	1,2-Dichloropropane	5	(b)	31	(b)	31	26	22	(b)	20	(b)
44.	Bromoform	30	(b)	(b)	(b)	(b)	14(c)	(b)	(b)	(b)	(b)
46.	2-Hexanone	25	(b)	2	(b)	12	89	(b)	(b)	(b)	(b)
47.	1,1,2,2-Tetrachloroethane	5	(b)	(b)	(b)	(b)	188(c)	(b)	(b)	(b)	(b)
50.	Chlorobenzene	20	46	50	72	53	39	42	31	54	115
51.	Ethylbenzene	5	62	67	(b)	79	85	81	47	74	109
	Total no. of spike compounds reported		2	5	1	4	7	3	2	3	2

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

(c) Compound was probably misidentified.

TABLE 29. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-7

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory[a]								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	600	114	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
24.	2-Chloroacrylonitrile	100	(b)	(b)	(b)	(b)	19	(b)	(b)	(b)	(b)
25.	1,1,1-Trichloroethane	100	16	25	60	(b)	22	28	41	(b)	3
33.	1,2-Dichloropropane	500	54	47	71	33	66	55	66	46	12
44.	Bromoform	100	(b)	42	75	15	7	(b)	(b)	(b)	13
46.	2-Hexanone	100	(b)	50	(b)	(b)	257	81	89	(b)	30
47.	1,1,2,2-Tetrachloroethane	600	43	25	53	33	51	38	29	39	8
50.	Chlorobenzene	100	51	30	84	39	46	55	63	66	10
51.	Ethylbenzene	400	58	20	78	36	51	61	66	90	(b)
	Total no. of spike compounds reported		6	7	6	5	8	6	6	4	6

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 30. RECOVERY OF VOLATILE COMPOUNDS FROM ILS-8

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	16000	127	(b)	(b)	58	(b)	(b)	103	(b)	(b)
24.	2-Chloroacrylonitrile	4000	143	174	(b)	105	203	91	130	(b)	116
25.	1,1,1-Trichloroethane	24000	132	110	124	55	(b)	97	138	119	135
33.	1,2-Dichloropropane	4000	102	88	103	88	59	68	71	(b)	(b)
44.	Bromoform	4000	126	100	107	44	155	82	69	(b)	51
46.	2-Hexanone	24000	73	66	97	104	162	75	94	(b)	90
47.	1,1,2,2-Tetrachloroethane	16000	106	99	99	115	96	94	87	35	45
50.	Chlorobenzene	20000	103	94	111	88	30	91	116	90	176
51.	Ethylbenzene	4000	106	91	109	89	55	88	90	(b)	203
	Total no. of spike compounds reported		9	8	7	9	7	8	9	3	7

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 31. RECOVERY OF SEMIVOLATILE COMPOUNDS FROM ILS-2

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a) Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
5.	4-Chlorotoluene	600	38	56	13	24	35	125	93	62	88
12.	Bis(2-chloroethyl)ether	500	24	67	48	27	30	143	83	58	77
13.	2-Chlorophenol	600	36	69	50	22	36	116	77	51	82
15.	2,4,6-Trimethylpyridine	600	47	64	(b)	(b)	(b)	305	99	96	67
16.	1,4-Dichlorobenzene	100	29	46	15	17	9	(b)	(b)	45	73
22.	Acetophenone	100	(b)	149	23	75	74	108	127	109	158
25.	Hexachloroethane	500	41	51	19	39	(b)	44	67	82	70
28.	4-t-Butylpyridine	100	45	76	22	44	(b)	(b)	(b)	(b)	(b)
33.	2,4-Dimethylphenol	100	(b)	94	(b)	57	56	(b)	(b)	61	87
36.	Propiophenone	400	(b)	92	16	39	56	95	72	54	83
43.	4-Chloroaniline	600	(b)	40	6	26	34	32	(b)	344	6
50.	Quinoline	500	24	82	46	53	61	73	71	69	87
51.	Bis(2-chloroethoxy)ethane	100	(b)	68	(b)	51	55	(b)	(b)	60	75
56.	4-Chloro-2-methylaniline	100	(b)	112	(b)	21	(b)	(b)	(b)	34	69
57.	4-Chlorobenzoic acid	500	(b)	85	(b)	55	(b)	(b)	(b)	96	(b)
64.	1-Chloronaphthalene	100	(b)	98	(b)	42	(b)	(b)	(b)	50	(b)
65.	4-Methylquinoline	100	(b)	102	22	46	(b)	(b)	134	57	185
66.	2-Ethylnaphthalene	500	46	137	24	57	59	84	94	71	99
69.	4-Bromobenzoic acid	100	(b)	75	(b)	28	(b)	(b)	(b)	(b)	(b)
74.	1,3-Dinitrobenzene	500	(b)	71	(b)	29	19	(b)	30	35	49
76.	2,6-Dinitrotoluene	100	(b)	91	(b)	40	(b)	(b)	(b)	56	68
77.	3-Nitroaniline	500	(b)	92	(b)	56	48	(b)	(b)	(b)	129
80.	2,4-Dinitrophenol	400	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
84.	4-Nitrophenol	100	(b)	59	(b)	50	(b)	(b)	(b)	(b)	(b)
85.	Pentachlorobenzene	100	(b)	84	26	49	76	(b)	86	96	84
98.	2-Chloro-4-nitroaniline	100	(b)	78	(b)	45	(b)	(b)	(b)	(b)	(b)
100.	Hexachlorobenzene	600	42	114	24	56	87	85	94	80	109

(continued)

TABLE 31. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
117.	Anthraquinone	600	27	129	19	47	77	81	55	72	98
118.	Fluoranthene	100	46	104	28	50	64	81	74	84	109
120.	2-Methylanthraquinone	100	(b)	130	20	50	78	(b)	63	61	103
121.	Pyrene	400	50	105	26	54	68	98	98	81	110
123.	4,4'-DDD	100	30	62	30	59	110	(b)	(b)	88	91
125.	4,4'-DDT	400	23	60	17	63	96	(b)	43	69	91
126.	Triphenyl phosphate	600	21	180	24	63	161	(b)	97	42	109
132.	Tri-(p-tolyl) phosphate	100	(b)	16	19	63	80	(b)	85	(b)	90
137.	Dibenzocarbazole	100	(b)	171	(b)	35	85	65	(b)	(b)	189
	Total no. of spike compounds reported		16	35	22	34	24	15	20	28	29

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 32. RECOVERY OF SEMIVOLATILE COMPOUNDS FROM ILS-3

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory[a]								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
5.	4-Chlorotoluene	800	30	83	97	(b)	337	81	95	70	84
12.	Bis(2-chloroethyl)ether	200	14	90	(b)	(b)	(b)	139	88	81	86
13.	2-Chlorophenol	800	15	24	16	(b)	(b)	25	19	20	(b)
15.	2,4,6-Trimethylpyridine	800	22	97	(b)	(b)	15	602	1100	46	270
16.	1,4-Dichlorobenzene	200	23	62	74	(b)	272	50	85	51	59
22.	Acetophenone	1000	12	76	10	(b)	122	55	54	49	58
25.	Hexachloroethane	200	37	84	102	(b)	705	41	73	64	62
28.	4-t-Butylpyridine	200	19	54	64	(b)	(b)	(b)	(b)	37	57
33.	2,4-Dimethylphenol	200	(b)	(b)	(b)	(b)	138	(b)	(b)	(b)	(b)
36.	Propiophenone	200	(b)	54	16	(b)	413	39	47	29	35
43.	4-Chloroaniline	800	(b)	(b)	(b)	(b)	39	(b)	(b)	(b)	(b)
50.	Quinoline	200	21	95	(b)	(b)	609	60	84	67	68
51.	Bis(2-chloroethoxy)ethane	1200	23	103	66	47	412	77	81	40	75
56.	4-Chloro-2-methylaniline	200	(b)	18	(b)	(b)	(b)	68	(b)	(b)	(b)
57.	4-Chlorobenzoic acid	200	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
64.	1-Chloronaphthalene	1200	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
65.	4-Methylquinoline	1200	23	110	99	(b)	494	98	(b)	72	(b)
66.	2-Ethylnaphthalene	200	(b)	(b)	(b)	(b)	357	(b)	(b)	(b)	(b)
69.	4-Bromobenzoic acid	1200	(b)	21	(b)	(b)	(b)	(b)	(b)	(b)	(b)
74.	1,3-Dinitrobenzene	200	(b)	(b)	(b)	(b)	633	(b)	(b)	(b)	122
76.	2,6-Dinitrotoluene	1200	(b)	(b)	89	(b)	449	(b)	46	48	64
77.	3-Nitroaniline	200	(b)	(b)	(b)	(b)	419	(b)	(b)	(b)	(b)
80.	2,4-Dinitrophenol	200	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
84.	4-Nitrophenol	1000	(b)	(b)	38	(b)	(b)	(b)	(b)	(b)	(b)
85.	Pentachlorobenzene	200	17	45	65	(b)	228	(b)	58	46	51
98.	2-Chloro-4-nitroaniline	1200	(b)	8	(b)	(b)	133	(b)	(b)	(b)	(b)
100.	Hexachlorobenzene	800	38	92	135	(b)	539	79	100	87	102

(continued)

TABLE 32. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory[a]								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
117.	Anthraquinone	800	27	95	117	(b)	557	101	96	(b)	93
118.	Fluoranthene	1000	32	77	72	(b)	269	67	75	63	71
120.	2-Methylanthraquinone	200	(b)	120	111	(b)	506	110	107	(b)	102
121.	Pyrene	200	(b)	(b)	(b)	(b)	223	(b)	(b)	6	(b)
123.	4,4'-DDD	1000	37	110	109	(b)	549	82	107	136	113
125.	4,4'-DDT	200	30	109	106	(b)	1740	(b)	79	109	102
126.	Triphenyl phosphate	800	23	117	100	(b)	578	79	92	92	99
132.	Tri-(p-tolyl) phosphate	200	(b)	67	90	(b)	522	(b)	116	(b)	(b)
137.	Dibenzocarbazole	1200	(b)	(b)	(b)	(b)	32	(b)	(b)	3	(b)
	Total no. of spike compounds reported		18	24	20	1	27	18	20	21	20

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

(c) There apparently is a calculation error in this set of data from Lab 5.

TABLE 33. RECOVERY OF SEMIVOLATILE COMPOUNDS FROM ILS-4

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5(d)	Lab 6	Lab 7	Lab 8	Lab 9
5.	4-Chlorotoluene	1900	59	80	85	39	176	51	(b)	51	86
12.	Bis(2-chloroethyl)ether	11400	53	77	41	49	273	73	34	60	79
13.	2-Chlorophenol	1900	64	88	97	44	471	65	(b)	62	81
15.	2,4,6-Trimethylpyridine	1900	93	104	(b)	153	(b)	(b)	(b)	142	(b)
16.	1,4-Dichlorobenzene	7600	49	62	76	40	133	50	50	49	78
22.	Acetophenone	1900	53	104	98	43	287	69	(b)	58	83
25.	Hexachloroethane	11400	52	64	76	34	259	57	42	45	80
28.	4-t-Butylpyridine	7600	63	73	136	30	187	61	(b)	42	115
33.	2,4-Dimethylphenol	7600	62	91	106	43	307	79	(b)	62	83
36.	Propiophenone	9500	47	99	115	39	271	80	(b)	57	101
43.	4-Chloroaniline	1900	51	66	114	(b)	242	163	(b)	(b)	(b)
50.	Quinoline	11400	16	23	25	11	63	18	(b)	14	19
51.	Bis(2-chloroethoxy)ethane	1900	60	88	118	38	290	61	(b)	56	75
56.	4-Chloro-2-methylaniline	7600	78	84	125	(b)	130	25	33	(b)	162
57.	4-Chlorobenzoic acid	11400	67	(b)	75	22	591	96	(b)	93	32
64.	1-Chloronaphthalene	1900	62	93	(b)	47	(b)	(b)	(b)	64	(b)
65.	4-Methylquinoline	1900	75	96	42	46	264	103	(b)	55	342
66.	2-Ethylnaphthalene	11400	8	9	9	6	42	8	(b)	7	10
69.	4-Bromobenzoic acid	1900	47	(b)	80	(b)	(b)	(b)	(b)	(b)	(b)
74.	1,3-Dinitrobenzene	11400	(b)	104	82	27	371	57	(b)	50	99
76.	2,6-Dinitrotoluene	1900	67	100	93	(b)	396	63	(b)	37	83
77.	3-Nitroaniline	11400	66	87	122	29	374	52	(b)	(b)	143
80.	2,4-Dinitrophenol	9500	2	1	(b)	(b)	(b)	26	(b)	31	46
84.	4-Nitrophenol	1900	77	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
85.	Pentachlorobenzene	7600	63	88	81	58	270	69	48	68	95
98.	2-Chloro-4-nitroaniline	1900	49	99	68	(b)	415	37	(b)	31	(b)
100.	Hexachlorobenzene	1900	52	111	103	55	327	65	(b)	64	90

(continued)

TABLE 33. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5(d)	Lab 6	Lab 7	Lab 8	Lab 9
117.	Anthraquinone	1900	39	132	110	50	364	59	(b)	71	95
118.	Fluoranthene(c)	1900	51	102	101	58	176	68	49	69	111
120.	2-Methylanthraquinone	7600	42	127	79	44	339	77	(b)	63	116
121.	Pyrene(c)	9500	31	69	57	42	126	48	42	49	82
123.	4,4'-DDD	1900	52	86	112	51	331	48	(b)	123	88
125.	4,4'-DDT	9500	33	89	62	50	351	44	(b)	61	90
126.	Triphenyl phosphate	1900	31	176	99	(b)	336	66	(b)	25	90
132.	Tri-(p-tolyl) phosphate	7600	160	223	98	(b)	394	71	39	29	94
137.	Dibenzocarbazole	1900	(b)	(b)	(b)	(b)	16	(b)	(b)	(b)	(b)
	Total no. of spike compounds reported		34	32	31	26	31	31	8	30	29

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

(c) The recoveries are corrected for the amount present in the unspiked sample.

(d) There apparently is a calculation error in this set of data from Lab 5.

TABLE 34. RECOVERY OF SEMIVOLATILE COMPOUNDS FROM ILS-5

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
5.	4-Chlorotoluene	4	(b)	7	(b)	(b)	(b)	(b)	(b)	(b)	(b)
12.	Bis(2-chloroethyl)ether	24	(b)	55	20	30	(b)	35	32	29	6
13.	2-Chlorophenol	4	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
15.	2,4,6-Trimethylpyridine	4	(b)	13	(b)	(b)	(b)	(b)	249	(b)	(b)
16.	1,4-Dichlorobenzene	16	(b)	12	10	6	(b)	7	10	7	2
22.	Acetophenone	4	(b)	61	20	23	(b)	23	(b)	27	5
25.	Hexachloroethane	24	(b)	12	8	6	(b)	4	9	5	1
28.	4-t-Butylpyridine	16	(b)	9	38	5	8	18	(b)	22	7
33.	2,4-Dimethylphenol	16	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
36.	Propiophenone	20	(b)	79	59	28	36	50	39	42	8
43.	4-Chloroaniline	4	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
50.	Quinoline	24	(b)	29	40	20	22	35	35	41	6
51.	Bis(2-chloroethoxy)ethane	4	(b)	77	85	(b)	(b)	31	(b)	40	8
56.	4-Chloro-2-methylaniline	16	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
57.	4-Chlorobenzoic acid	24	(b)	(b)	(b)	23	(b)	42	(b)	35	8
64.	1-Chloronaphthalene	4	(b)	58	(b)	29	(b)	(b)	61	49	(b)
65.	4-Methylquinoline	4	(b)	15	24	9	(b)	22	68	(b)	17
66.	2-Ethylnaphthalene	24	44	85	42	40	(b)	49	49	58	8
69.	4-Bromobenzoic acid	4	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
74.	1,3-Dinitrobenzene	24	(b)	116	56	23	(b)	40	39	39	8
76.	2,6-Dinitrotoluene	4	(b)	69	90	(b)	(b)	(b)	61	38	8
77.	3-Nitroaniline	24	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
80.	2,4-Dinitrophenol	20	(b)	9	8	(b)	(b)	12	(b)	34	7
84.	4-Nitrophenol	4	(b)	(b)	183	(b)	(b)	(b)	(b)	(b)	(b)
85.	Pentachlorobenzene	16	(b)	92	73	37	39	(b)	53	71	9
98.	2-Chloro-4-nitroaniline	4	(b)	80	(b)	(b)	(b)	(b)	(b)	(b)	(b)
100.	Hexachlorobenzene	4	(b)	92	74	31	(b)	35	55	58	8

(continued)

TABLE 34. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
117.	Anthraquinone	4	(b)	88	68	18	140	28	46	53	6
118.	Fluoranthene	4	61	101	122	22	159	38	65	57	9
120.	2-Methylanthraquinone	16	(b)	96	60	22	(b)	48	45	43	6
121.	Pyrene	20	33	92	47	22	53	41	49	50	7
123.	4,4'-DDD	4	(b)	85	108	40	172	32	85	94	8
125.	4,4'-DDT	20	21	104	50	45	(b)	37	41	85	8
126.	Triphenyl phosphate	4	(b)	89	86	39	(b)	38	58	35	(b)
132.	Tri-(p-tolyl) phosphate	16	(b)	154	77	35	53	(b)	67	17	9
137.	Dibenzocarbazole	4	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
	Total no. of spike compounds reported		4	29	24	22	9	21	21	24	13

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 35. RECOVERY OF SEMIVOLATILE COMPOUNDS FROM ILS-6

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
5.	4-Chlorotoluene	20	19	55	(b)	(b)	(b)	(b)	(b)	6	(b)
12.	Bis(2-chloroethyl)ether	20	(b)	45	(b)	(b)	(b)	(b)	(b)	21	(b)
13.	2-Chlorophenol	20	58	69	58	(b)	(b)	(b)	(b)	19	(b)
15.	2,4,6-Trimethylpyridine	20	(b)	60	(b)	(b)	(b)	(b)	(b)	(b)	(b)
16.	1,4-Dichlorobenzene	100	17	47	22	25	4	53	33	7	34
22.	Acetophenone	20	20	42	(b)	(b)	(b)	17	(b)	16	(b)
25.	Hexachloroethane	20	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
28.	4-t-Butylpyridine	100	44	68	40	39	15	35	(b)	16	83
33.	2,4-Dimethylphenol	100	57	82	63	42	30	55	(b)	19	50
36.	Propiophenone	120	16	41	19	17	17	25	(b)	6	25
43.	4-Chloroaniline	20	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
50.	Quinoline	20	27	20	16	(b)	(b)	29	(b)	(b)	(b)
51.	Bis(2-chloroethoxy)ethane	80	42	26	55	39	(b)	52	(b)	12	44
56.	4-Chloro-2-methylaniline	100	33	76	13	(b)	(b)	40	(b)	(b)	(b)
57.	4-Chlorobenzoic acid	20	(b)	(b)	(b)	(b)	(b)	(b)	(b)	50	150
64.	1-Chloronaphthalene	80	29	86	(b)	(b)	63	66	48	225	(b)
65.	4-Methylquinoline	80	26	49	27	24	(b)	68	(b)	19	123
66.	2-Ethylnaphthalene	20	39	102	29	48	(b)	71	(b)	24	75
69.	4-Bromobenzoic acid	80	58	11	41	18	(b)	47	(b)	(b)	(b)
[illegible].	1,3-Dinitrobenzene	20	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
76.	2,6-Dinitrotoluene	80	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
77.	3-Nitroaniline	20	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
80.	2,4-Dinitrophenol	120	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
84.	4-Nitrophenol	20	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
85.	Pentachlorobenzene	100	28	89	41	50	31	69	68	22	67
98.	2-Chloro-4-nitroaniline	80	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
100.	Hexachlorobenzene	20	(b)	100	46	48	(b)	58	(b)	(b)	(b)

(continued)

TABLE 35. (Continued)

Cpd. No.	Compound	Amount Spiked, µg/g	Percent Recovery Reported by Given Laboratory(a)								
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
117.	Anthraquinone	20	(b)	56	18	(b)	(b)	30	(b)	(b)	(b)
118.	Fluoranthene	20	28	74	40	49	63	79	82	25	94
120.	2-Methylanthraquinone	100	17	67	24	(b)	24	47	39	14	54
121.	Pyrene	120	30	100	20	63	49	81	84	25	97
123.	4,4'-DDD	20	78	311	107	198	85	184	(b)	68	262
125.	4,4'-DDT	120	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
126.	Triphenyl phosphate	20	(b)	160	29	41	(b)	(b)	(b)	(b)	(b)
132.	Tri-(p-tolyl) phosphate	100	30	116	43	66	56	71	91	23	81
137.	Dibenzocarbazole	80	33	195	(b)	36	90	93	(b)	(b)	(b)
	Total no. of spike compounds reported		21	27	20	16	12	21	7	19	14

(a) Average of the values reported for all analytical runs (maximum of 3) in which the compound was detected and quantified.

(b) Not determined because the compound was not detected and quantified in any of the three analytical runs performed by the laboratory.

TABLE 36. MATRIX OF TOTAL VOLATILE COMPOUNDS REPORTED

Sample	Laboratory Number									Total Per Sample
	1	2	3	4	5	6	7	8	9	
ILS-2	8	6	8	8	8	8	9	8	8	71
ILS-3	6	7	7	8	8	8	8	7	8	67
ILS-4	5	7	7	6	8	4	8	2	3	51
ILS-5	4	7	4	3	3	6	3	4	3	37
ILS-6	2	5	1	4	7	3	2	3	2	29
ILS-7	6	7	6	5	8	6	6	4	6	54
ILS-8	9	8	7	9	7	8	9	3	7	67
Total Per Laboratory	40	47	40	43	49	44	45	31	37	

TABLE 37. MATRIX OF TOTAL SEMIVOLATILE COMPOUNDS REPORTED

Sample	Laboratory Number									Total Per Sample
	1	2	3	4	5	6	7	8	9	
ILS-2	16	35	22	34	24	15	20	28	29	223
ILS-3	18	24	20	1	27	18	20	21	20	168
ILS-4	34	32	31	26	31	31	8	8	29	252
ILS-5	4	29	24	22	9	21	21	21	13	167
ILS-6	21	27	20	16	12	21	7	7	14	157
Total Per Laboratory	93	147	117	99	103	106	76	122	105	

However, caution should be used in attributing poor results with particular samples as a failure of the method. Appreciable compound losses may have occurred prior to analysis as a result of spiking procedures, degradation during storage or handling losses.

A presentation of percent detection data, arranged according to specific compound, for each waste sample is provided in Table 38 for volatile compounds and Table 39 for semivolatile compounds. Interpretation of these two data tables provides information regarding the effect of compound and further information regarding effect of sample. In addition, the data are identified as either low spike level (underlined values) or high spike level. The average percent of reported compounds was higher for both volatile and semivolatile compounds spiked at the high level (73 and 70 percent respectively). The low level spikes were reported 57 percent of the time for volatile determinations and 47 percent for semivolatile determinations. The most difficult waste samples are also apparent using these data, namely ILS-5 and ILS-6 for VOA and ILS-3, ILS-5 and ILS-6 for semivolatile analyses.

The ability of a laboratory to detect specific volatile and semivolatile compounds may be discerned from the data presented in Tables 40 and 41. Labs 3 and 8 reported the fewest volatile compounds. Lab 7 reported only 42 percent of the semivolatile compounds compared to 81 percent for Lab 2 and an average reporting value of 59 percent for all the participants.

The most troublesome compounds may be identified by comparing data presented in Tables 38 through 41. The best VOA results were obtained for high boiling compounds such as chlorobenzene, tetrachloroethane, and ethylbenzene. The more polar compounds, propionitrile, chloroacrylonitrile and hexanone, were not detected as often as the less polar compounds. The semivolatile compounds most suitable for determination by the methodology were aromatic hydrocarbons and halocarbons such as pyrene, fluoranthene, and hexachlorobenzene. Poor results were generated for benzoic acids and nitrophenols.

The laboratory-to-laboratory variability for detection, identification and quantification of the volatile and semivolatile compounds may provide key information for methodology applicability and revisions. In some cases, errors in calculation are the primary cause of variability and some misunderstanding of reporting requirements may have occurred. Trends that were apparent include:

- Lab 2 consistently reported more SV and VOA compounds
- Lab 7 reported the fewest SV compounds
- Lab 8 reported the fewest VOA compounds
- Lab 5 reported high recoveries for both SV and VOA compounds
- Lab 4 reported lower recoveries for SV compounds and the most variability in total detection on a sample-to-sample basis

The causes for some of the trends may be discernable by implementing a more exhaustive approach to data interpretation.

The most dramatic difference in application of the analysis methods was experienced with the prescreening protocols. The amount of tetraglyme extract analyzed for each waste by specific participants is presented in Table 42. The volumes vary by three orders of magnitude for samples ILS-4, ILS-5, ILS-6 and ILS-8. The laboratory reporting fewest VOA compounds, Lab 8, consistently

TABLE 38. EFFECT OF COMPOUND, SAMPLE AND SPIKE LEVEL ON DETECTABILITY OF VOLATILE COMPOUNDS

No.	Compound	Percent of Data Reported For Given Sample[a][b] ILS-2	ILS-3	ILS-4	ILS-5	ILS-6	ILS-7	ILS-8	Average Percent Low[c]	High[d]	Total[e]
12.	Propionitrile	11	0	22	11	0	11	26	4	18	12
24.	Chloroacrylonitrile	100	96	4	11	4	4	78	24	67	42
25.	1,1,1-Trichloroethane	100	93	78	11	7	78	89	65	65	65
33.	1,2-Dichloropropane	100	96	100	56	48	100	78	75	88	83
44.	Bromoform	100	85	56	67	4	56	89	67	63	65
46.	2-Hexanone	89	52	37	11	26	52	89	38	68	51
47.	1,1,2,2-Tetrachloroethane	89	93	67	100	4	100	100	62	92	79
50.	Chlorobenzene	96	96	100	89	100	100	100	97	97	97
51.	Ethylbenzene	100	96	89	41	89	89	89	77	95	87
	Average	87	79	61	44	31	66	82	57	73	64

(a) The maximum number of analytical runs for which data could be reported for each sample was 27 (3 replicates x 9 laboratories).

The percent of data reported = $\frac{\text{total number of analytical runs for which data were reported x 100}}{27}$

(b) Percent of data reported for compounds spiked at the low level are underlined.
(c) Average of the percents of data reported for samples spiked at the low level.
(d) Average of the percents of data reported for samples spiked at the high level.
(e) Average of the percents of data reported for all samples.

TABLE 39. EFFECT OF COMPOUND, SAMPLE AND SPIKE LEVEL ON SEMIVOLATILE COMPOUNDS

No.	Compound	Percent of Data Reported For Given Sample[a][b] ILS-2	ILS-3	ILS-4	ILS-5	ILS-6	Average Percent Low[c]	High[d]	Total[e]
6.	4-Chlorotoluene	96	89	89	11	33	44	93	64
12.	Bis(2-chloroethyl)ether	100	67	96	78	22	45	91	73
13.	2-Chlorophenol	100	67	89	0	44	44	84	60
15.	2,4,6-Trimethylpyridine	59	78	37	22	11	23	69	41
16.	1,4-Dichlorobenzene	70	89	100	78	93	80	90	86
22.	Acetophenone	89	89	89	67	44	72	89	76
25.	Hexachloroethane	89	85	100	78	0	43	89	70
28.	4-t-Butylpyridine	44	56	89	67	85	50	80	68
33.	2,4-Dimethylphenol	56	4	89	0	89	30	59	48
36.	Propiophenone	89	78	89	89	89	78	89	87
43.	4-Chloroaniline	74	11	56	0	11	22	43	30
50.	Quinoline	100	78	89	89	44	61	93	80
51.	Bis(2-chloroethoxy) ethane	56	100	89	56	78	67	89	76
56.	4-Chloro-2-methylaniline	41	22	78	0	44	32	41	37
57.	4-Chlorobenzoic acid	33	0	78	44	22	11	52	35
64.	1-Chloronaphthalene	33	0	44	44	59	40	30	36
65.	4-Methylquinoline	63	67	89	67	78	73	73	73
66.	2-Ethylnaphthalene	100	11	89	89	78	45	93	73
69.	4-Bromobenzoic acid	22	11	22	0	96	15	54	30
74.	1,3-Dinitrobenzene	63	19	78	78	0	10	73	48
76.	2,6-Dinitrotoluene	44	56	78	52	0	58	28	46
77.	3-Nitroaniline	44	7	78	0	0	4	41	26
80.	2,4-Dinitrophenol	0	0	56	44	0	0	33	20
84.	4-Nitrophenol	11	11	11	11	0	8	11	9
85.	Pentachlorobenzene	74	78	100	78	100	76	93	86
98.	2-Chloro-4-nitroaniline	22	15	59	11	0	31	8	21
100.	Hexachlorobenzene	100	89	89	78	44	70	95	80
117.	Anthraquinone	100	78	89	81	33	68	89	76

(continued)

TABLE 39. (Continued)

No.	Compound	Percent of Data Reported For Given Sample[a][b] ILS-2	ILS-3	ILS-4	ILS-5	ILS-6	Average Percent Low[c]	High[d]	Total[e]
118.	Fluoranthene	100	89	100	93	100	98	89	96
120.	2-Methylanthraquinone	78	67	89	78	89	73	85	80
121.	Pyrene	100	22	100	100	100	22	100	84
123.	4,4'-DDD	78	89	89	81	89	84	89	85
125.	4,4'-DDT	85	74	89	89	0	74	66	67
126.	Triphenyl phosphate	89	89	78	59	33	57	89	70
132.	Tri-(p-tolyl) phosphate	63	41	89	70	85	52	81	70
137.	Dibenzocarbazole	56	11	11	0	52	22	32	26
	Average	67	51	77	52	48	47	70	59

[a] The maximum number of analytical runs for which data could be reported for each sample was 27 (3 replicates x 9 laboratories).

$$\text{The percent of data reported} = \frac{\text{total number of analytical runs for which data were reported} \times 100}{27}$$

[b] Percent of data reported for compounds spiked at the low level are underlined.

[c] Average of the percents of data reported for samples in which the compound was spiked at the low level.

[d] Average of the percents of data reported for samples in which the compound was spiked at the high level.

[e] Average of the percents of data reported for all samples.

TABLE 40. EFFECT OF LABORATORY ON DETECTABILITY OF VOLATILE COMPOUNDS

Cpd. No.	Compound	Percent of Data Reported by Given Laboratory(a)								
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
12.	Propionitrile	29	0	14	5	14	0	43	0	0
24.	2-Chloroacrylonitrile	43	57	29	43	52	38	43	29	43
25.	1,1,1-Trichloroethane	71	95	71	57	57	67	71	43	57
33.	1,2-Dichloropropane	86	100	86	86	76	95	71	86	57
44.	Bromoform	29	86	86	71	76	52	71	43	71
46.	2-Hexanone	29	38	29	71	86	67	67	14	57
47.	1,1,2,2-Tetrachloroethane	86	67	86	71	90	81	86	71	71
50.	Chlorobenzene	100	95	100	100	86	95	100	100	100
51.	Ethylbenzene	100	100	71	90	90	95	86	57	71
	Average	64	72	56	68	71	67	72	51	60

(a) The maximum number of analytical runs for which data could be reported for each sample was 21 (3 replicates x 7 laboratories).

$$\text{The percent of data reported} = \frac{\text{total number of analytical runs for which data were reported} \times 100}{27}$$

TABLE 41. EFFECT OF LABORATORY ON DETECTABILITY OF SEMIVOLATILE COMPOUNDS

Cpd. No.	Compound	Percent of Data Reported by Given Laboratory[(a)]								
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
6.	4-Chlorotoluene	80	100	60	40	53	60	40	80	60
12.	Bis(2-chloroethyl)ether	60	100	60	60	33	80	80	100	80
13.	2-Chlorophenol	80	80	80	40	40	60	40	80	40
15.	2,4,6-Trimethylpyridine	60	100	0	20	20	40	53	40	40
16.	1,4-Dichlorobenzene	80	100	100	80	53	80	80	100	100
22.	Acetophenone	73	100	80	60	60	100	40	100	80
25.	Hexachloroethane	60	80	80	60	33	80	80	80	80
28.	4-t-Butylpyridine	80	100	100	80	47	60	0	67	80
33.	2,4-Dimethylphenol	40	60	40	60	60	40	0	60	60
36.	Propiophenone	40	100	100	80	100	100	53	100	100
43.	4-Chloroaniline	20	60	40	20	60	40	0	13	20
50.	Quinoline	80	100	80	60	80	100	60	80	80
51.	Bis(2-chloroethoxy) ethane	60	100	80	80	60	80	20	100	100
56.	4-Chloro-2-methylaniline	40	80	40	20	20	60	20	13	40
57.	4-Chlorobenzoic acid	20	20	20	60	20	40	0	80	60
64.	1-Chloronaphthalene	40	80	0	60	7	20	40	80	0
65.	4-Methylquinoline	60	100	100	80	40	80	33	80	80
66.	2-Ethylnaphthalene	80	80	80	80	60	80	40	80	80
69.	4-Bromobenzoic acid	40	60	40	40	0	20	0	0	0
74.	1,3-Dinitrobenzene	0	60	40	60	47	40	40	60	80
76.	2,6-Dinitrotoluene	20	60	60	20	40	20	40	73	80
77.	3-Nitroaniline	20	40	20	40	53	20	0	0	40
80.	2,4-Dinitrophenol	20	40	13	0	0	40	0	27	40
84.	4-Nitrophenol	20	20	40	20	0	0	0	0	0
85.	Pentachlorobenzene	60	100	100	80	93	40	100	100	100
98.	2-Chloro-4-nitroaniline	20	80	20	20	20	20	0	7	0
100.	Hexachlorobenzene	60	100	100	80	60	100	60	80	80

(continued)

TABLE 41. (Continued)

Cpd. No.	Compound	Percent of Data Reported by Given Laboratory[a]								
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9
117.	Anthraquinone	60	100	100	60	67	100	60	60	80
118.	Fluoranthene	100	100	100	80	87	100	100	100	100
120.	2-Methylanthraquinone	40	100	100	60	80	80	80	80	100
121.	Pyrene	80	80	80	80	100	80	80	100	80
123.	4,4'-DDD	80	100	100	80	87	80	60	80	100
125.	4,4'-DDT	80	80	80	60	47	40	60	80	80
126.	Triphenyl phosphate	60	100	100	60	60	60	60	67	60
132.	Tri-(p-tolyl) phosphate	40	100	100	60	60	40	100	47	80
137.	Dibenzocarbazole	20	40	0	40	67	40	0	7	20
	Average	52	81	65	55	50	59	42	64	63

[a] The maximum number of analytical runs for which data could be reported for each sample was 21 (3 replicates x 7 laboratories).

$$\text{The percent of data reported} = \frac{\text{total number of analytical runs for which data were reported} \times 100}{27}$$

TABLE 42. AMOUNT OF TETRAGLYME EXTRACT ANALYZED FOR THE DETERMINATION OF VOLATILE COMPOUNDS

Laboratory	Volume of Tetraglyme Extract of Given Waste Analyzed, µL[(a)]						
	ILS-2	ILS-3	ILS-4	ILS-5	ILS-6	ILS-7	ILS-8
Lab 1	20	3	2	200	200	10	1
Lab 2	5	5	250	2000	2000	100	1
Lab 3	10	1	3	30	15	10	0.2
Lab 4	10	3	25	200	200	10	0.2
Lab 5	5	20	5	50	200	50	10
Lab 6	30	10	5	200	200	30	5
Lab 7	(b)	(b)	(b)	(b)	(b)	(b)	(b)
Lab 8	1	1	3	200	200	4	0.04
Lab 9	6	3	0.2	100	3	60	0.06

(a) The volume given is that portion of the initial tetraglyme extract representing 1g of waste per 20 mL of extract. In order to obtain the amount of sample represented by the smaller volumes, the extract was diluted with tetraglyme. For example, 1 µL of the initial extract may have been obtained by using 20 µL of a 1:20 dilution of the initial extract.

(b) Not reported.

used a smaller volume of tetraglyme extract for the purge and trap part of the method. The laboratories reporting the highest percent of VOA data (Labs 2 and 5 generally used large volumes of extract. Lab 7 did not report these data so interpretation of performance could not be made.

For the semivolatile screening method, variations of up to three orders of magnitude were observed for the methylene chloride extract concentration factor as shown in Table 43. Lab 2 which reported the most semivolatile compounds used the higher concentration factors. The poor performance by Lab 7 for SV determination could not be assessed, for this parameter, since the concentration factor was not reported. Additional information regarding the criteria used by each of the laboratories to make the decisions affecting the VOA extract volume and SV concentration factor is essential for standardizing the application of the tested methods.

In addition to the comparative data presented in tabular form in this report, additional comparisons could be made by fully using the large quantity of information generated for the program. Statistical analyses excluding obvious outliers were beyond the scope of the effort reported here, however, valuable information for decision making could be gleaned by further evaluation of the data.

TABLE 43. METHYLENE CHLORIDE EXTRACT CONCENTRATION FACTOR USED FOR SEMIVOLATILE COMPOUND DETERMINATION

Laboratory	Concentration Factor Used For Methylene Chloride Extract of Given Waste Analyzed(a)					
	ILS-2	ILS-3	ILS-4	ILS-5	ILS-6	ILS-9
Lab 1	1	1	1	10	25	50
Lab 2	100	3	1	50	50	150
Lab 3	3	1	1	100	25	40
Lab 4	25	0.1	0.1	100	100	(c)
Lab 5	4	1	1	50	4	4
Lab 6	1	1	0.2	100	12	50
Lab 7	(b)	(b)	(b)	(b)	(b)	(b)
Lab 8	2	2	0.2	100	15	100
Lab 9	2	1	0.2	100	4	30

(a) The initial methylene chloride extract representing 1 g of waste per 50 mL of extract was concentrated by the listed factor prior to analyses. Concentration factors less than one indicate that the initial extract was diluted accordingly.

(b) Not reported.

(c) This sample was not analyzed by Lab 4.

REFERENCES

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3. "Purgeables -- Method 624", Federal Register, Vol. 44, 3 Dec. 1973, p. 69532.

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APPENDIX A

METHOD FOR THE DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS IN SOLID WASTES

Battelle - Columbus Laboratories - January, 1982

METHOD FOR THE DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS IN SOLID WASTES

1. Scope and Application

1.1 This method covers the determination of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 This method is applicable to the determination of most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols including nitrophenols.

1.4 The detection limit of the method for determining an individual compound is estimated to be approximately 1 µg/g (wet weight). For samples which contain more than 1 mg/g of total solvent extractable materials, the detection limit should be proportionately higher.

1.5 This method is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2. Summary of Method

2.1 A measured weight of sample, 3.0 g wet weight, is neutralized and sonified with 150 mL of methylene chloride. Anhydrous sodium sulfate is added to bind the water present. A portion of the methylene chloride supernatant is concentrated and analyzed by GC/MS using a fused silica capillary column. Qualitative identification is performed using the retention time of the compound and the relative abundance of three or more characteristic ions. Quantitative analysis is performed using an internal standard technique with a single characteristic ion.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and sample processing hardware that produces discrete artifacts and/or elevated baselines in the total ion current profiles. All of these problems must be demonstrated to be absent under the conditions of the analysis by routinely analyzing laboratory reagent blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing it with the last solvent used. Heating in a muffle furnace at 450°C for 5 to 15 hours is recommended whenever feasible. Alternatively detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation cf dust or other contaminants.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems.

3.2 Matrix interferences may be caused by components that are coextracted from the sample but are not normally of interest. The most common of such components are petroleum-derived naphthenes, high molecular weight polymeric components, and long-chain components such as waxes and triglycerides. The extent of such matrix interferences will vary considerably from sample to sample. A cleanup procedure using gel permeation chromatography has been incorporated into the method for certain cases to remove long-chain and high-molecular-weight material. No cleanup procedure is available for the removal of naphthenes. When such matrix interferences are present, the sample extract is diluted and the detection limit is increased proportionately. Many of the matrix interferences are solvent-extractable nonvolatile components which necessitate the more frequent cleaning of the GC injection port and the more frequent removal of the injection end of the GC capillary column.

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be minimized by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 All operations involving the use of methylene chloride, including the extraction of the waste sample, filtration of the extract, and concentration of the extract, must be performed in a fume hood. Care should be taken to avoid the skin contact with methylene chloride.

5. Apparatus

5.1 Sampling equipment - Glass screw-cap vials or jars of at least 100 mL capacity. Screw caps must be Teflon lined.

5.2 Glassware

5.2.1 Beaker - 400 mL

5.2.2 Centrifuge tubes - approximately 200-mL capacity, glass with screw cap (Corning No. 1261 or equivalent). Screw caps must be fitted with Teflon liners.

5.2.3 Concentrator tube, Kuderna-Danish - 25 mL, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent extract evaporation.

5.2.4 Evaporative flask, Kuderna-Danish 250-mL (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish - Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish - Two-ball micro (Kontes K-569001-0219 or equivalent).

5.4 Micro syringe - 100 µL (Hamilton No. 84858 or equivalent).

5.5 Weighing pans, micro - approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

5.6 Boiling chips - approximately 10-40 mesh carborundum (A. H. Thomas No. 1590-D30 or equivalent). Heat to 450°C for 5-10 hr. or extract with methylene chloride.

5.7 Water bath - Heated, capable of temperature control (±2°C). The bath should be used in a hood.

5.8 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.9 Microbalance - Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

5.10 Sonifier - 375 watt, fitted with a 1/2-inch probe and a half-wave extension, capable of pulsed operation at variable power settings. (Heat Systems-Ultrasonics Sonicator Model W-375 with No. 200 1/2-inch disrupter horn and No. 406-HW-050-T half-wave extender, or equivalent).

5.11 Centrifuge - Capable of accommodating 200-mL glass centrifuge tubes.

5.12 pH meter and electrodes - Capable of accurately measuring pH to ±0.2 pH unit.

5.13 Spatula - Having a metal blade 1-2 cm in width.

5.14 Heat lamp - 250 watt reflector-type bulb (GE No. 250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

5.15 Gas chromatograph/mass spectrometer system

5.15.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

5.15.2 Column - 30 m x 0.25 mm bonded-phase silicone coated fused silica capillary column (J W Scientific DB-5 or equivalent).

5.15.3 Mass spectrometer - Capable of scanning from 40 to 450 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

5.15.4 Data system - A computer system must be interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.16 Gel permeation chromatography system.

5.16.1 Chromatographic column - 600 mm x 25 mm I.D. glass column fitted for upward flow operation.

5.16.2 Bio-Beads S-X8 - 80 g per column.

5.16.3 Pump - capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

5.16.4 Injector - with 5-mL loop

5.16.6 Strip chart recorder.

5.16.5 Ultraviolet detector - 254 mm

6. Reagents

6.1 Reagent water - Reagent water is defined as water in which no interference is observed at the method detection limit for each compound of interest.

6.2 Potassium phosphate, tribasic (K_3PO_4) - Granular (ACS).

6.3 Phosphate buffer, $4\underline{M}$, - 2.0 moles of Na_2HPO_4 and 2.0 moles of NaH_2PO_4 dissolved in reagent water and diluted to 1000 mL. The solution is very temperature sensitive; it must be checked carefully before using and, if necessary, warmed to redissolve any crystals that may have formed.

6.4 Phosphoric acid (H_3PO_4) - 85% aqueous solution (ACS).

6.5 Sodium sulfate, anhydrous (Na_2SO_4) - Powder (ACS).

6.6 Methylene chloride - Distilled-in-glass quality (Burdick and Jackson, or equivalent).

6.7 Internal standards - D_5-bromobenzene, D_8-naphthalene, D_{10}-biphenyl, D_{10}-acenaphthene, D_{10}-phenanthrene, D_{10}-pyrene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene.

6.7 Column performance standards - D_5-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol.

6.8 Surrogate standards - Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

6.9 Decafluorotriphenylphosphine (DFTPP).

6.10 GPC calibration solution - Methylene chloride containing 100 mg of corn oil, 20 mg of di-n-octyl phthalate, 3 mg of coronene, and 2 mg of sulfur per 100 mL.

7. Calibration

7.1 A multiple internal standard calibration procedure as described by Sauter, et al(1) is used. To use this approach, the analyst must select five or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurements of the internal standard are not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standards are added to all calibration standards and all sample extracts analyzed by GC/MS. Column performance standards, and a mass spectrometer tuning standard are included in the internal standard solution used.

7.1.1 A set of five or more internal standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to at least one of the internal standards. The following internal standards are recommended for general use: D_5-bromobenzene, D_8-naphthalene, D_{10}-biphenyl, D_{10}-acenaphthene, D_{10}-phenanthrene, D_{10}-pyrene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene.

7.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standards to assess the column performance of the GC/MS system. The following column performance standards are recommended for general use: D_5-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol. These compounds can also serve as internal standards if appropriate and the internal standards recommended in Section 7.1.1 can serve as column performance standards if appropriate.

7.1.3 Decafluorotriphenylphosphine (DFTPP) is used to tune the mass spectrometer on each workshift.

7.1.4 Prepare the internal standard solution by dissolving in 50.0 mL of methylene chloride 10.0 mg of each standard compound specified in Sections 7.1.1, 7.1.2, and 7.1.3. The resulting solution will contain each standard at a concentration of 200 µg/mL. A solution containing 500 g/mL of each standard can be prepared by using 5 percent benzene in methylene chloride as the solvent.

7.2 Prepare calibration standards at a minimum of three concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. Each calibration standard should be mixed with an appropriate amount of the internal standard solution. One of the calibration standards should be at a concentration of two to five times the method detection limit, 1 to 10 g/mL; one should be at a concentration near, but below the concentration that causes saturation of the mass spectrometer; and, the third should be at a concentration in the middle of this working range of the GC/MS system.

7.3 Analyze 1 to 2 µL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate response factors (RF) for each compound using equation 1.

Eq. 1 $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard; the internal standard chosen should be such that the relative retention time of the compound is within the range of 0.80 to 1.20 and as close as possible to 1.00.

C_{is} = Concentration of the internal standard, (µg/mL).

C_s = Concentration of the compound to be measured (µg/mL).

If the RF value over the working range is constant ($<$ 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ± 20% of the response factor used for quantification of the sample concentrations.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must peform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 10.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery, (s), for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery, (s/R x 100), must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give a concentration, in the final extract used for GC/MS analysis, that is equal to the concentration, of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 10 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 10.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data, so qualified, to ensure that the frequency remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic components, respectively.

8.5 Before processing any samples, the analyst must demonstrate, through the analysis of a process blank, that all glassware and reagent interferences are under control. Each time a set of samples is extracted, or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP
- Response factors of the internal standards and column performance standards relative to D_{10}-phenanthrene
- Relative retention times of column performance standards relative to the closest internal standard
- Peak area intensity and absolute retention time of D_{10}-phenanthrene.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

9.2 The samples must be refrigerated at 4°C from the time of collection until extraction.

9.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

10. Sample Extraction

10.1 The extraction procedure involves sonification of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. The particle size of all samples, except those comprised of nonporous inorganic particles, should be reduced to less than 0.1 mm diameter before extraction. A glass mortar and pestle are recommended for grinding the sample.

10.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 200-mL centrifuge tube. Add 15 mL of methylene chloride and 15 mL of water.

10.1.2 Sonify the mixture for two minutes by inserting the sonifier horn 0.5 to 1.0 cm below the surface and using a power setting of 5 and a 50 percent pulsed-duty cycle.

10.1.3 Transfer the contents of the centrifuge tube to a 400-mL beaker using 50 mL of methylene chloride followed by 150 mL of water as rinses.

10.1.4 Adjust the pH of the mixture to 7.0 ± 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter. Record the volume of acid or base required.

10.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-mL centrifuge tube. Add 15 mL of methylene chloride. Spike the sample with surrogate standards as described in Section 8.4. Add 1.0 mL of 4 M phosphate buffer, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 10.1.4. For example, if the acid requirement in Section 10.1.4 was 2.0 mL of 0.4 M H_3PO_4, the amount of 4 M H_3PO_4 needed would be 0.2 mL.

10.3 Sonify the mixture for 1 minute by inserting the sonifier horn 0.5 to 1.0 cm below the surface and using a power setting of 5 and a 50 percent pulsed-duty cycle. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20 to 30°C. Add 135 mL of methylene chloride, adjust the position of the sonifier horn to 0.5 to 1.0 cm below the surface and repeat the sonification for 1 minute. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add, all at once, an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g for each mL of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 10.2. Immediately cap the centrifuge tube and shake vigorously for 1 minute. Insert the sonifier horn 0.5 to 1.0 cm below the surface and sonify for 2 minutes as described above. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. filter the supernatant required for Sections 10.4, 10.5, and 10.7 (at least 2 mL) through a 0.2 µm Teflon filter.

10.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 10.3 Transfer 0.1 mL of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for one minute to allow the solvent to evaporate, and then weigh on a microbalance. If the residue weight of the 0.1-mL aliquot is less than 0.05 mg, concentrate 25 mL of the supernatant to 1.0 mL and obtain a residue weight on 0.1 mL of the concentrate. For the concentration step use a 25-mL evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65°C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 2 if concentration was not required or Equation 3 if concentration was required.

Eq. 2. $$\frac{\text{mg of Residue}}{\text{g of Sample}} = \frac{\text{Residue Wt., mg, of 0.1 mL of Supernatant}}{0.002}$$

Eq. 3. $$\frac{\text{mg of Residue}}{\text{g of Sample}} = \frac{\text{Residue Wt., mg, of 0.1 mL of Concd. Supernatant}}{0.05}$$

10.5 If the TSEC of the sample (as determined in Section 10.4 is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-mL aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-mL aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g use 100 mL of the supernatant. Perform the concentration by transferring the supernatant aliquot to a K-D flask fitted into a 25-mL concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65°C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 mL, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 minutes while cooling. Remove the Snyder column and rinse the flask and the lower joint of the flask into the concentrator tube with methylene chloride to bring the volume to 10.0 mL. Mix the concentrator tube contents by inserting a stopper and inverting several times.

10.6 Analyze the concentrate from Section 10.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 10.3 using gas chromatography. Use a 30-m x 0.25 mm bonded-phase silicone coated fused silica capillary column under the chromatographic conditions described in Section 13. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal or external standard (e.g., phenanthrene) at a concentration of 50-100 μg/mL.

10.7 If the optimum concentration determined in Section 10.6 is 20 mg of residual material per mL or less proceed to Section 10.8. If the optimum concentration is greater than 20 mg of residual material per mL and if the TSEC if greater than 50 mg/g, apply the GPC cleanup procedure described in Section 11. For the GPC cleanup concentrate 90 mL of the supernatant from Section 10.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 10.5 and concentrate to a final volume of 15.0 mL. Stop the concentration prior to reaching 15.0 mL if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out).

10.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 10.5 or an aliquot of the supernatant from Section 10.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 11.3 to obtain 1.0 mL of a solution having the optimum concentration, as described in Section 10.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 mL with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 mL as described in Section 10.4. Do not let the volume in the concentrator tube go below 0.6 mL at any time. Stop the concentration prior to reaching 1.0 mL if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 mL) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add a volume of the internal standard solution that contains 50 μg each of the internal standards, column performance standards, and DFTPP, to 1.0 mL of the final concentrate and save for GC/MS analysis as described in Section 13. Calculate the concentration in the original sample that is represented by the internal standard using Equation 4 if an aliquot of the concentrate from Section 10.5 was used in Section 10.8. Equation 5 if an aliquot of the supernatant from Section 10.3 was used in Section 10.8, or Equation 6 if an aliquot of the GPC concentrate from Section 11.3 was used in Section 10.8.

$$\text{Eq. 4} \quad \frac{\mu\text{g of Int. Std.}}{\text{g of Sample}} = \frac{50}{3} \times \frac{150}{V_{s(10.5)}} \times \frac{10}{V_{c(10.8)}} \times \frac{\text{Final Vol., mL}}{1}$$

$$\text{Eq. 5} \quad \frac{\mu\text{g of Int. Std.}}{\text{g of Sample}} = \frac{50}{3} \times \frac{150}{V_{s(10.8)}} \times \frac{\text{Final Vol., mL}}{1}$$

$$\text{Eq. 6} \quad \frac{\mu\text{g of Int. Std.}}{\text{g of Sample}} = \frac{50}{3} \times \frac{150}{V_{s(10.7)}} \times \frac{V_F}{V_{GPC(10.7)}} \times \frac{\text{Final Vol., mL}}{1}$$

where:

V_S = Volume of supernatant from Section 10.3 used in Sections 10.5, 10.8, or 10.7

$V_{C(10.8)}$ = Volume of concentrate from Section 10.5 used in Section 10.8.

$V_{F(10.7)}$ = Final volume of concentrate in Section 10.7.

V_{GPC} = Volume of GPC concentrate from Section 11.3 used in Section 10.8.

Use this calculated value for the quantification of individual compounds as described in Section 15.2.

11. Cleanup Using Gel Permeation Chromatography

11.1 Prepare a 600 mm x 25 mm I.D. gel permeation chromatography (GPC) column using a slurry containing 80 g of Bio-Beads S-X8 that have been allowed to swell in methylene chloride for at least 4 hours. Prior to initial use, rinse the column with methylene chloride at 1 mL/min for 16 hours to remove any traces of contaminants. Calibrate the system by injecting 5 mL of the GPC calibration solution, eluting with methylene chloride at 5 mL/min for 50 minutes and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

11.2 Inject a 5-mL aliquot of the concentrate from Section 10.7 onto the GPC column and elute with methylene chloride at 5 mL/min for 50 minutes. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-mL aliquot of the concentrate from Section 10.7 and combine the fractions collected.

11.3 Concentrate the combined GPC fractions to 10.0 mL as described in Section 10.5. Estimate the TSEC of the concentrate as described in Section 10.4. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis as described in Section 10.6.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that the tuning sensitivity and overall performance of the system are acceptable. The quality control protocols required for the fused silica capillary column GC/MS analyses are described in a separate report.(2)

12.2 The following instrumental parameters are required for all performance tests and for all sample analyses:

Electron Energy - 70 volts (nominal)
Mass Range - 40 to 450 amu
Scan Time - 0.75 second per scan.

12.3 The mass spectrometer must be tuned to achieve all of the key ion criteria for the mass spectrum of DFTPP(3) given in Table 1 when a solution containing 50 µg/mL of DFTPP is injected into the GC/MS system. If the DFTPP analysis meets the criteria in Table 1, the sample analyses are considered valid. Otherwise, the analyst must retune the instrument to meet the Table 1 criteria, followed by reanalysis of the sample in question.

12.4 The electron multipier of the mass spectrometer must be adjusted such that the injection of a solution containing 20 µg/mL of phenanthrene or D_{10}-phenanthrene will give a response that is approximately 20 times the detection limit but less than one-tenth of the value that causes serious saturation of the mass spectrometer.

12.5 The sensitivity of the GC/MS system must be such that a response factor of at least 0.05 relative to D_{10}-phenanthrene is obtained for pentachlorophenol and 2,4-dinitroaniline when a solution containing 50 µg/mL of each component is injected.

13. GC/MS Analysis

13.1 Analyze the 1-mL concentrate from Section 10.8 by GC/MS using a 30 m x 0.25 mm bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial Column Temperature Hold - 30°C for 4 minutes
Column Temperature Program - 30-300°C at 8 degrees/min
Final Column Temperature Hold - 300°C for 10 minutes
Injector Temperature - 280°C
Transfer Line Temperature - 300°C
Injector - Grob-type, splitless
Sample Volume - 1 µL
Carrier Gas - Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

13.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.3 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store the extracts at 4°C protected from light in screw cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

14.1.1 The characteristic ions for each compound of interest must maximize in the same scan or within one scan of each other.

14.1.2 The retention time must fall within ± 15 seconds of the retention time of the authentic compound..

14.1.3 The relative peak heights of the characteristic ions in the EICPs must fall within ± 20% of the relative intensities of these ions in a reference mass spectrum.

15. Quantitative Determination

15.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

15.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 7.

$$\text{Eq. 7 Concentration, } \mu g/g = \frac{\mu g \text{ of Int. Std.}}{g \text{ of Sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{RF}$$

where:

$\frac{\mu g \text{ of Int. Std.}}{g \text{ of Sample}}$ = Internal standard concentration factor calculated in Section 10.8

A_s = area of the primary characteristic ion of the compound being quantified

A_{is} = area of the primary characteristic ion of the internal standard

RF = response factor of the compound being quantified determined in Section 7.3; use a response factor of 1.0 for the quantification of an unknown compound.

15.2 Report results in micrograms per gram without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

15.3 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of mass 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	greater than 1% of mass 198
441	present but less than mass 443
442	greater than 40% of mass 198
443	17-23% of mass 442

16. References

1. Sauter, A. D., Betowski, L. D., Smith, T. R., Strickler, V. A., Beimer, B. G., Colby, B. N., and Wilkinson, J. E., "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants", J. High Resolut. Chromatogr. Chromotogr. Commun., 4, 366 (1981).

2. "Quality Control Protocol for the Fused Silica Capillary Column Gas Chromatography/Mass Spectrometry Determination of Semivolatile Organic Compounds", Battelle Columus Laboratories revision of a September 1981 priority pollutant protocol prepared by Acurex Corporation for U.S. Environmental Protection Agency, Environmental Monitoring and Systems Laboratory, Las Vegas, NV 89114, November, 1981.

3. Eichelberger, J. W., Harris, L. E., and Budde, W. L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems", Anal. Chem., 47, 995 (1975).

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APPENDIX B

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOLID WASTES

Battelle - Columbus Laboratories - November 10, 1981

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOLID WASTES

1. Scope and Application

1.1 This method covers the determination of volatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous waste, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 The detection limit of the method for determining an individual compound is estimated to be approximately 1 µg/g (wet weight). For samples which contain more than 1 mg/g of total volatile material, the detection limit should be proportionately higher.

1.4 The method is based upon a purge and trap, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.5 This method is restricted to use by, or under the supervision of analysts experienced in the use of purge and trap systems and gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.

2. Summary of Method

A portion of solid waste is dispersed in tetraglyme to dissolve the volatile organic constituents. A portion of the tetraglyme solution is combined with water in a specially designed purging chamber. An inert gas is then bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components which are then detected with a mass spectrometer.(1-2)

3. Interferences

3.1 Low molecular weight impurities in tetraglyme can be volatilized during the purging procedure. Thus, the tetraglyme employed in this method must be purified before use and stabilized to prevent peroxide formation as described in Section 6.2.

3.2 Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.3. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.4 Contamination by carry-over can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. After each use, the purging chamber is cleaned as described in Section 11.4.3. The trap and other parts of the system are also subject to contamination; therefore, frequent additional heating and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be minimized by whatever means available; this warning is particularly important when handling reference compounds. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals used in applying this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified(3-5) for the information of the analyst.

4.2 The following volatile organic compounds which may be determined by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Whenever primary standards containing any of these or other toxic compounds are prepared, the operation should be performed in a hood. A NIOSH/MSHA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial - 25 mL capacity or larger, equipped with a screw cap (Pierce 13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry for one hour at 105°C before use.

5.1.2 Septum - Teflon-faced silicone (Pierce 12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105°C for one hour before use.

5.2 Purge and trap device - The purge and trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are now commercially available.

5.2.1 The purging chamber must be designed to accept 5-mL or 25-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum amounts of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.2), 15 cm of silica gel (Section 6.3.3). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber must be capable of rapidly heating the trap to 180°C within 30 seconds. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C. The desorber design, illustrated in Figure 2, meets these criteria.

5.2.4 The purge and trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 Gas chromatograph/mass spectrometer system

5.3.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

5.3.2 Column - 2 m x 2 mm ID stainless or glass, packed with 1 percent SP-1000 on 60/80 mesh Carbopack B or equivalent.

5.3.3 Mass spectrometer - Capable of scanning from 40 to 250 amu every 7 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

5.3.4 GC/MS interface - Any GC to MS interface that gives accceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 10) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.3.5 Data system - A computer system must be interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.4 Sample Transfer Implements - Implements are required to transfer portions of solid, semi-solid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle or no needle attached. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the closed end of the barrel of a glass hypodermic syrings.

5.5 Syringes - 5-mL and 25-mL gas-tight with shut-off valve, equipped with narrow-bore needle, at least 15 cm in length.

5.6 Micro syringes - 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1000-µL. These syringes should be equipped with narrow-bore needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

5.7 Centrifuge tubes - 50-mL round bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-mL graduation (Kimble #45212) or equivalent).

5.8 Centrifuge - Capable of accommodating 50-mL glass tubes.

5.9 Bottle - 15-mL, screw-cap, Teflon cap liner.

5.10 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.11 Rotary evaporator - equipped with Teflon-coated seals (Buchi Rotavapor R-100, or equivalent).

5.12 Vacuum pump - mechanical, two stage.

5.13 Sonifier - 375-watt, fitted with a 1/2-in probe and a half-wave extension, capable of pulsed-operation at variable power settings (Heat Systems - Ultrasonics Sonicator Model W-375 with 200 1/2-in disruptor horn and 406-HW-050-T half wave extender, or equivalent).

6. Reagents

6.1 Reagent Water - Reagent water is defined as water in which no interferent is observed at the method detection limit for the compounds of interest.

6.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon lined septum and cap.

6.2 Reagent Tetraglyme. Reagent tetraglyme is defined as tetraglyme for which no interferences are observed at the method detection limit for the compounds of interest.

6.2.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich 17, 240-5 or equivalent) is purified by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 and other suppliers). Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed is a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90 to 100°C and vacuum is maintained at <10 mm Hg for at least two hours using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a Dry Ice/methanol bath. Cool the tetraglyme to ambient temperature and add 0.1 mg/mL of 2.6-di-tert-butyl-4-methylphenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw-cap bottle in an area that is free of solvent vapors.

6.2.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, a reagent water/tetraglyme blank must be analyzed.

6.3 Trap Materials

6.3.1 2,6-Diphenylene oxide polymer - 60/80 mesh Tenax, chromatographic grade or equivalent.

6.3.2 Methyl silicone packing - 3% OV-1 on 60/80 mesh Chromosorb-W or equivalent.

6.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

6.4 Calibration standards; stock solutions - Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds in tetraglyme using assayed liquids or gases as appropriate.

6.4.2.1 Liquids - Using a 100-µL syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the tetraglyme without contacting the neck of the flask.

6.4.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with a reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the tetraglyme meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the tetraglyme.

6.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards in methanol may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.4.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20°C and protect from light.

6.4.5 Prepare fresh standards weekly for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicate a problem.

6.5 Calibration standards; secondary dilution solutions - Using stock solutions described in Section 6.5, prepare secondary dilution standards in tetraglyme that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration solutions prepared as described in Section 7.3.2 will bracket the working range of the analytical system(2). Secondary dilution standards should be stored with minimal headspace.

6.6 Surrogate standards - Surrogate standards are added to all samples and calibration solutions; the compounds employed for this purpose are 1,2-dibromotetrafluoroethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and m-bromobenzotrifluoride added to each sample to assess the effect of the sample matrix on recovery efficiency. Prepare tetraglyme solutions of the surrogate standards using the procedures described in Sections 6.5 and 6.6. The concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added assuming a 100 percent recovery of the surrogate standards.

6.7 Internal standards - In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D_4-1,2-dichloroethane, D_6-benzene, and D_5-ethylbenzene are recommended as internal standards covering a wide boiling point range.

6.8 4-Bromofluorobenzene (BFB) - BFB is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

6.9 Internal standard solution - Using the procedures described in Sections 6.5 and 6.6, prepare a tetraglyme solution containing BFB and each internal standard at a concentration of 20.0 µg/mL.

6.10 Sodium monohydrogen phosphate - 2.0 M in distilled water.

6.11 n-Nonane and n-dodecane, 98+ percent purity.

6.12 n-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

7. Calibration

7.1 Assemble a purge and trap device that meets the specifications in Section 5.2 and connect the device to a GC/MS system. Condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Prior to use, daily condition the trap for 10 minutes while backflushing at 180°C.

7.2 Operate the gas chromatograph using the conditions described in Section 11.4 and operate the mass spectrometer using the conditions described in Section 10.2.

7.3 Calibration Procedure:

7.3.1 Conduct calibration procedures using a minimum of three concentration levels for each calibration standard. One of the concentration levels should be two to five times the method detection limit (5 to 50 ng); one should be at a level near but below the concentration that causes saturation of the mass spectrometer; and the third should be at a level in the middle of this working range of the GC/MS system.

7.3.2 Prepare a solution containing the required concentrations of calibration standards, including surrogate standards, to 5 mL of reagent water contained in a 5-mL gas-tight syringe having a shut-off valve and fitted with a 15-cm narrow-bore needle. Add a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (see Section 6.6) to the reagent water using a microsyringe. When discharging the contents of the microsyringe be sure that the end of the syringe needle is well beneath the surface of the water. Similarly, add 12.5 µL of the internal standard solution (see Section 6.10). Add the contents of the 5-mL syringe to the purging device by inserting the needle as far as possible through the septum of the purging device and discharging the contents slowly.

7.3.3 Conduct the purge and analysis procedure as described in Sections 11.4. Tabulate the area response of the primary characteristic ion against concentration for each compound including the internal standards. Calculate response factors (RF) for each compound using Equation 1.

Eq. 1 $$RF = (A_s C_{is})/(A_{is}\ C_s)$$

where:

A_s = Area of the primary characteristic ion for the compound to be measured

A_{is} = Area of the primary characteristic ion of the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, versus RF.

7.3.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards, analyzed immediately before and after a set of samples, must be within ± 20% of the response factor used for quantification of the sample concentrations.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to continuously monitor laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must peform the following operations using a representative sample as a check sample.

8.2.2 Analyze four aliquots of the unspiked check sample according to the method in Section 11.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in tetraglyme at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples by adding the spiking solution to the tetraglyme used for the extraction. Analyze the spiked aliquots according to the method in Section 11.

8.2.4 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery, (s), for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery, (s/R x 100), must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give an amount in the purge apparatus that is equal to the amount of the internal standard assuming a 100 percent recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction described in Section 11.1 to estimate the major volatile compounds content and determining the amount of extract to be analyzed as described in Section 11.3.2. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that the frequency remains at or below 5 percent. Four surrogate standards, namely 1,2-dibromodifluorethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and m-bromobenzotrifluoride, are recommended for general use to monitor recovery of volatile compounds varying in volatility and polarity.

8.5 Each day, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Storage

9.1 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to obtain minimum headspace or void space. Vials contaiing liquid sample should be stored in an inverted position.

9.2 All samples must be refrigerated from the time of collection to the time of analysis, and should be protected from light.

10. Daily GC/MS Performance Tests

10.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB(6).

10.2 The BFB performance test requires the following instrumental parameters.

Electron Energy: 70 volts (nominal)
Mass Range: 40 to 250 amu
Scan Time: to give at least 6 scans per peak but not to exceed 7 seconds per scan.

10.3 Bleed BFB vapor into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of BFB given in Table 1.

10.4 BFB is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for BFB during the analysis of a sample differs by more than 20% from that observed during the analysis of the calibration solution, then the analysis in question is considered invalid. The instrument must then be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

10.5 The peak intensity of D_6-benzene is used to monitor the mass spectrometer sensitivity. The peak intensity for D_6-benzene observed during each sample analysis must be between 0.7 and 1.4 times the D_6-benzene peak intensity observed during the applicable calibration runs. For example, if the peak intensity of D_6-benzene observed during calibration was 170,000 area counts, then each subsequent sample or blank must give a D_6-benzene peak intensity of between 120,000 and 240,000 area counts. If the D_6-benzene peak intensity is outside of the specified range, the sample must be reanalyzed. If the peak intensity is again outside the specified range, the analyst must investigate the cause of the variability in sensitivity and correct the problem.

11. Sample Extraction and Analysis

The analytical procedure involves extracting the sample with tetraethylene glycol dimethyl ether (tetraglyme) and analyzing a portion of the extract by a purge and trip GC/MS procedure. The amount of the extract to be taken for the GC/MS analysis is based on the estimated major volatile compounds content (MVCC) of the sample. The MVCC is estimated by extracting the sample with n-hexadecane and analyzing the n-hexadecane extract using gas chromatography.

11.1 The estimated MVCC is based on the area response relative to that of n-nonane for the five major components that elute prior to the retention time of n-dodecane. The response factor and the retention time of n-nonane are determined by analyzing a 2-µL aliquot of an n-hexadecane solution containing 100 µg/mL of n-nonane.

11.1.1 The GC analyses are conducted using a flame ionization detector and a 3 m x 2 mm I.D. glass column packed with 10% OV-101 on 100-120 mesh Chromosorb W-HP. The column temperature is programmed from 80°C to 280°C at 8 degrees per minute and held at 280°C for 10 minutes.

11.1.2 Determine the area response for n-nonane and divide by 100 to obtain the area response factor. Record the retention time of n-nonane.

11.1.3 Add 1.0 gm of sample to 20 mL of n-hexadecane and 2 mL of 0.5 M Na_2HPO_4 contained in a 50-mL glass centrifuge tube and cap securely with a Teflon-lined screw cap. Shake the mixture vigorously for one minute. If the sample does not disperse during the shaking process, sonify the mixture for two minutes by inserting the sonifier horn 1-2 cm below the surface of the hexadecane and using a power setting of 5 and a 25 percent pulsed duty cycle. Cap the tube tightly and allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

11.1.4 Analyze a 2-µL aliquot of the n-hexadecane supernatant using the conditions described in Section 11.1.1. Determine the total area response for the five major components that elute prior to the retention time of n-nonane and subtract any areas for the same five components that appear in an n-hexadecane blank. Using the 11.1.2, calculate the MVCC using Equation 2.

$$\text{Eq. 2} \quad \text{MVCC} = \frac{\text{MVCAR}_{\text{sample}} - \text{MVCAR}_{\text{blank}}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

MVCC = major volatile compounds content of the sample in µg/g.

$\text{MVCAR}_{\text{sample}}$ = major volatile compounds area response obtained for the sample

$\text{MVCAR}_{\text{blank}}$ = major volatile compounds area response

11.2 The transfer of an aliquot of the sample for extraction with tetraglyme should be made as quickly as possible to minimize loss of volatiles from the sample.

11.2.1 To a 50-mL glass centrifuge tube with Teflon-lined cap, add 40 mL of reagent tetraglyme. Add an appropriate volume of the surrogate standard solution; insert the needle of the syringe approximately 4 cm below the surface of the tetraglyme during the addition. Weigh the capped centrifuge tube and tetraglyme on an analytical balance.

11.2.2 Using an appropriate implement (see Section 5.4), transfer approximately 2 gm of sample to the tetraglyme in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the tetraglyme as quickly as possible. Take care not to touch the sample-transfer implement to the tetraglyme. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

11.2.3 Disperse the sample by vigorous agitation for one minute. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture for two minutes by inserting the sonifier horn 1-2 cm below the surface of the tetraglyme and using a power setting of 5 and a 25 percent pulsed duty cycle. Cap the tube tightly and allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

11.2.4 The sample extract may be stored for future analytical needs. If storage is desired, transfer the solution to a 10 mL screw cap vial with teflon cap liner. Store at -10 to -20°C, and protect from light.

11.3 Reagent water, internal standard solution, and the sample extract are added to a purging chamber that is conected to the purge and trap device and that has been flushed with helium during a seven-minute trap reconditioning step (see Section 11.4.4). The additions are made using an appropriate size syringe equipped with a 15-CM narrow-bore needle. Insert the needle through the septum of the purging device as far as possible.

11.3.1 Add 5.0 mL of reagent water to which 12.5 µL of the internal standard solution has been added (see Section 6.9) to the purging device. Insert the needle of the microsyringe approximately 4 cm below the surface of the water during the addition of the internal standard solution.

11.3.2 Inject an aliquot of the sample extract from Section 11.2.3 below the surface of the water in the purging device. The total quantity of the five major volatile compounds injected should not exceed approximately 2 µg. If the major volatile compound content (MVCC) of the sample as determined in Section 11.1.4 is 200 µg/g or less use a 200-µL aliquot of the sample aliquot. If the MVCC is greater than 200 µg/g, use an aliquot of the sample extract that contains 2 to 4 µg of the five major volatile compounds. Dilute the sample extract with tetraglyme as necessary to prepare a diluted extract that contains 10 to 400 µg/mL of the five major volatile compounds. The concentration (in µg/mL) of the five major volatile compounds in the sample extract can be calculated by dividing the MVCC by 20 times the dilution factor (DF). The volume (in µL) of the aliquot of the diluted extract to be taken can be calculated by dividing 20,000xDF by the MVCC and multiplying by 2 to 4. For example, if the MVCC is 14,000 µg/g and a DF of 10 is used, 20,000 DF/MVCC = 14.3; multiplying by 2 to 4 given 28.6 to 57.2; therefore, a 40-µL aliquot (representing 0.0002 g of original sample) would be an appropriate volume of the diluted extract to take for analysis. If the major volatile compounds are expected to be halogenated compounds, use only one fifth of the amount of the diluted extract determined above. If the MVCC is less than 200 µg/g and greater sensitivity is desired, use a large purging chamber containing 25-mL of reagent water and use a 1.0 mL aliquot of the sample extract. The volume of diluted extract to be taken for analysis can be used to determine the appropriate volume of surrogate standard solution to be used in Section 11.2.1. The appropriate volume of surrogate standard solution to add to the 2-gram sample can be calculated using Equation 4. Equation 4 is derived from Equation 3.

$$\text{Eq. 3} \quad V_{ss} = V_{0.25} \times \frac{Ve \times DF}{Va}$$

where:

V_{ss} = Appropriate volume, µL, of surrogate standard solution to add to a 2-gram sample.

$V_{0.25}$ = Volume of surrogate standard solution that contains 0.25 µg.

V_e = Volume of tetraglyme extract, µL, from original extraction of a 2-gram sample.

DF = Dilution factor.

V_a = Volume of diluted extract to be taken for analysis

Since $V_{0.25}$ equals 0.25 µg divided by the concentration, µg/µL, of the surrogate standard solution and V_e=40,000 µL, Equation 4 can be obtained.

$$\text{Eq. 4} \quad V_{ss} = \frac{0.25}{C_{ss}} \times \frac{40{,}000\ DF}{V_a} = \frac{10{,}000\ DF}{C_{ss} \times V_a}$$

where:

C_{ss} = Concentration, µg/µL, of the surrogate standard solution.

11.4 The sample in the purging device is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

11.4.1 Adjust the gas (helium) flow rate to 40 ± 2 mL/min. Set the purging device to purge and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

11.4.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column - 6 ft x 2 mm ID glass column packed with 1% SP-1000 on Carbopack B (60-80 mesh)

Temperature - Isothermal at 45°C for 3 minutes, then increased at 8°C per minute to 240°C, and maintained at 240°C for 15 minutes.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with helium at a flow rate of 30 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30°C or lower during the 4-minute desorb step and starting the GC program after the desorb step.

11.4.3 Return the purge trap device to the purge mode and continue acquiring GC/MS data.

11.4.4 Allow the trap to cool for 8 minutes. Replace the purging chamber with a clean purging chamber fitted with a new septum. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution, and distilled water and drying at 105°C.

11.4.5 Purge the trap at ambient temperature for 4 minutes. Recondition the trap by heating it to 180°C. Do not allow the trap temperature to exceed 180°C, since the sorption/desorption is adversely affected by heating the trap to higher temperatures. After heating the trap for approximately seven minutes, turn off the trap heater. When cool, the trap is ready for use with the next sample.

11.5 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 11.2.3.

12. Qualitative Identification

12.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

12.1.1 The characteristic ions of each compound of interest must maximize in the same scan or within one scan of each other.

12.1.2 The retention time must fall within ± 30 seconds of the retention time of the authentic compound.

12.1.3 The relative peak heights of the characteristic ions in the EICPSs must fall within ± 20% of the relative intensities of these ions in a reference mass spectrum.

13. Quantitative Determination

13.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

13.1.1 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 3.

Eq. 3 Concentration μg/g = $(A_s C_{is})/(A_{is})(RF)$

where:

A_s = Area of the primary characteristic ion of the compound to be measured.

A_{is} = Area of the primary characteristic ion of the internal standard.

C_{is} = Concentration of the internal standard in μg/g.

RF = Response factor of the compound being quantified determined in Section 7.3.3.

13.2 Report results in micrograms per gram without correction for recovering data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 If the surrogate standard recovery falls outside the control limits of Section 8.3, the data for all compounds in that sample must be labelled as suspect.

14. References

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2. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Measurement of Organic Pollutants in Water and Wastewater, C. E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publications 686, 1978.

3. "Carcinogens--Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publications No. 77-206, Aug. 1977.

4. "OSHA Safety and Health Standards, General Industry", (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. Budde, W. L., and J. W., Eichelberger. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories", EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, p. 16, April 1980.

TABLE 1. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 100% of mass 174
177	5 to 9% of mass 176

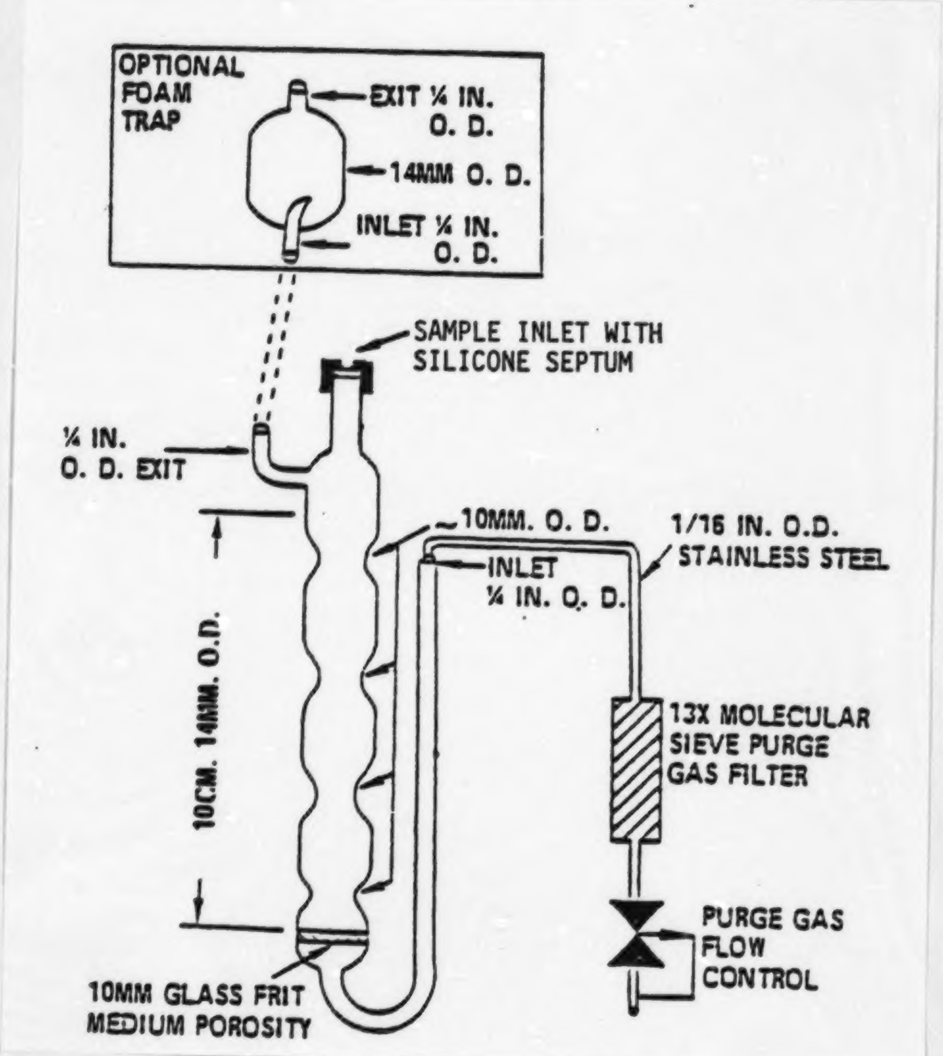

OPTIONAL
FOAM
TRAP
EXIT ¼ IN. O. D.
14MM O. D.
INLET ¼ IN. O. D.
SAMPLE INLET WITH SILICONE SEPTUM
¼ IN. O. D. EXIT
~10MM. O. D.
1/16 IN. O.D. STAINLESS STEEL
INLET ¼ IN. O. D.
10CM. 14MM. O.D.
13X MOLECULAR SIEVE PURGE GAS FILTER
PURGE GAS FLOW CONTROL
10MM GLASS FRIT MEDIUM POROSITY

Figure 1. Purging chamber.

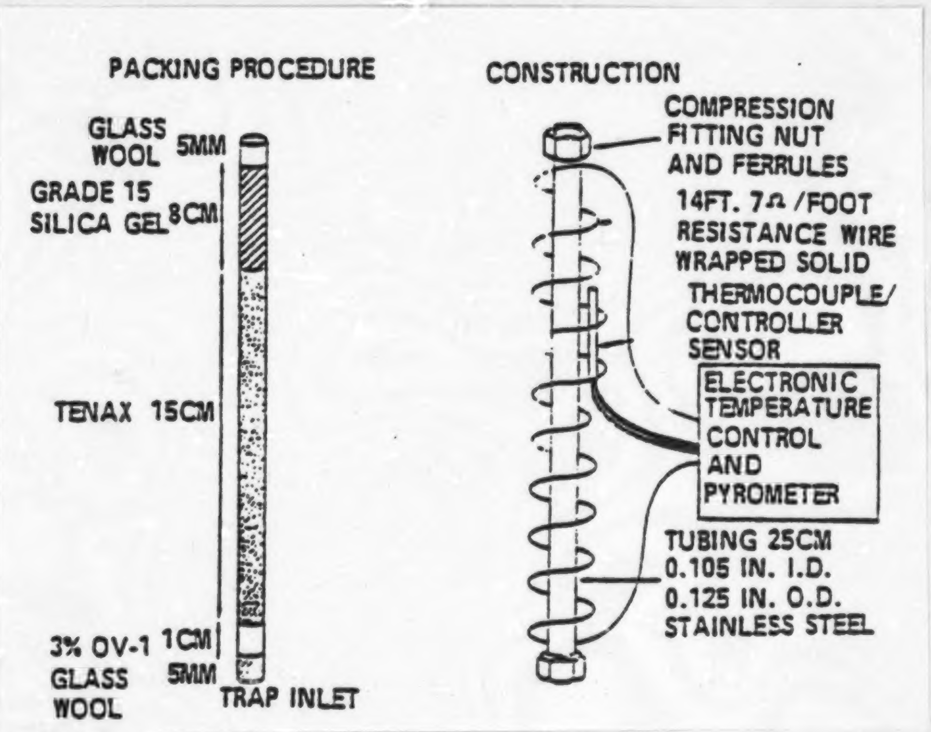
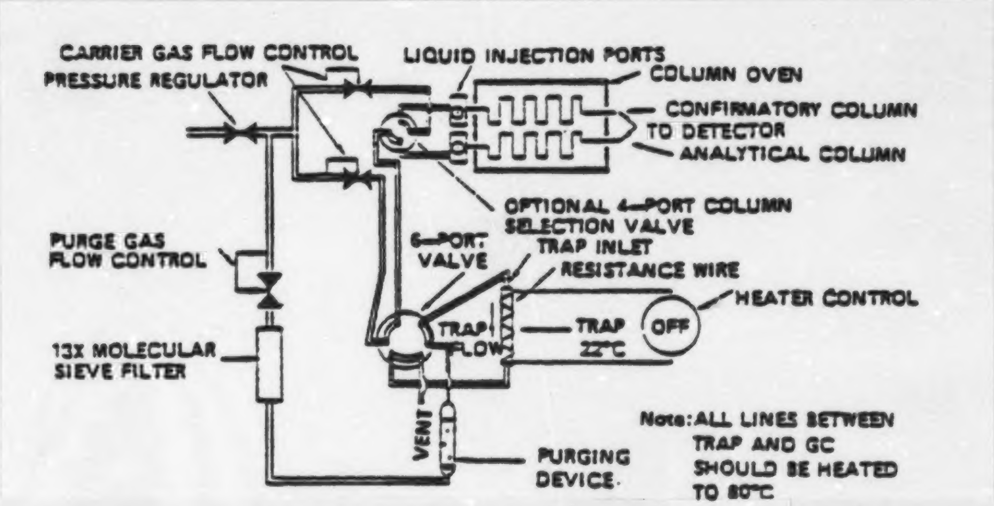
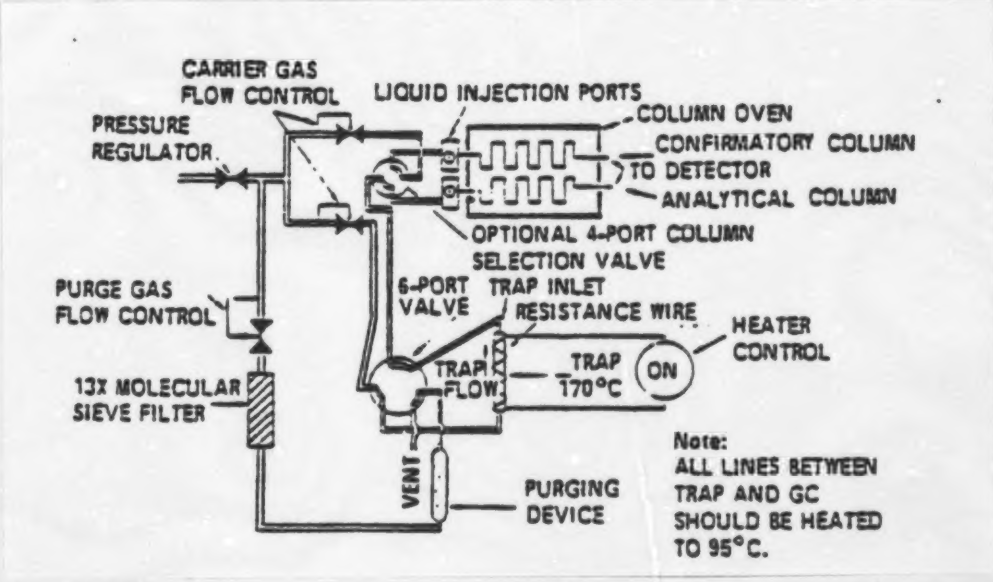

PACKING PROCEDURE
CONSTRUCTION
GLASS WOOL 5MM
GRADE 15 SILICA GEL 8CM
TENAX 15CM
3% OV-1 1CM
GLASS WOOL 5MM
TRAP INLET
COMPRESSION FITTING NUT AND FERRULES
14FT. 7Ω/FOOT RESISTANCE WIRE WRAPPED SOLID
THERMOCOUPLE/ CONTROLLER SENSOR
ELECTRONIC TEMPERATURE CONTROL AND PYROMETER
TUBING 25CM 0.105 IN. I.D. 0.125 IN. O.D. STAINLESS STEEL

Figure 2. Trap packings and construction to include desorb capability.


CARRIER GAS FLOW CONTROL
LIQUID INJECTION PORTS
PRESSURE REGULATOR
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN SELECTION VALVE
PURGE GAS FLOW CONTROL
6-PORT VALVE
TRAP INLET
RESISTANCE WIRE
HEATER CONTROL
TRAP
FLOW
TRAP 22°C
OFF
13X MOLECULAR SIEVE FILTER
VENT
PURGING DEVICE

Note: ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 80°C

Figure 3. Schematic of purge and trap device - purge mode.


CARRIER GAS FLOW CONTROL
LIQUID INJECTION PORTS
PRESSURE REGULATOR
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN SELECTION VALVE
PURGE GAS FLOW CONTROL
6-PORT VALVE
TRAP INLET
RESISTANCE WIRE
HEATER CONTROL
TRAP
FLOW
TRAP 170°C
ON
13X MOLECULAR SIEVE FILTER
VENT
PURGING DEVICE

Note:
ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 95°C.

Figure 4. Schematic of purge and trap device - desorb mode.

MK-139-82

APPENDIX C

QUALITY CONTROL PROTOCOL

QC Protocol for Fused Silica Capillary Columns

The QC Protocol presented here was developed by Acurex under the Direction of Mr. Drew Sauter, EPA-LV and modified by Battelle for application to this interlaboratory study. This protocol for the use of fused silica capillary columns must be followed when the method for the determination of semivolatile organic compounds is used. No deviations from this protocol are permitted.

QUALITY CONTROL PROTOCOL FOR THE FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS

Revision of September 1981 Acurex Corporation Protocol

For

Andrew D. Sauter
Environmental Protection Agency
Environmental Monitoring and Systems Laboratory
Las Vegas, Nevada 89114

By

Battelle Columbus Laboratories
Analytical Chemistry Section

1. SUMMARY

This protocol describes the use of fused silica capillary columns (FSCC) for analysis of the semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). The protocol gives column specifications, installation and operating details, and requirements for system calibration and retention time reproducibility. The quality control is based on multiple internal standards for column performance evaluation and tuning evaluation and on an initial multilevel calibration followed by regular single level calibration verifications.

The successive sections of this protocol describe the purpose of the protocol, the equipment requirements, column installation, operating conditions, sample injection, qualitative and quantitative identification, initial verification, ongoing QC activities, and documentation.

2. PURPOSE AND DESCRIPTION OF THE QC PROTOCOL

This protocol was written to support the efforts of the Environmental Monitoring Support Laboratory-Las Vegas (EMSL-LV) to standardize the use of FSCC. The operating conditions and the steps to be followed in implementing this quality control protocol are given in sufficient detail to obtain reproducible results. After installation of the FSCC, the GC/MS system is initially calibrated at three levels. Calibration checks at the middle level are repeated after the analysis of each set of up to eight samples or at least once daily, whichever is most frequent. Specifications for the calibration check results are given to determine the acceptability of the sample analysis data. Multiple internal standards are employed to verify system performance during each analysis.

3. EQUIPMENT REQUIREMENTS

3.1 Gas Chromatograph

Capable of isobaric splitless capillary column injection with quartz or glass-lined injection port; fused silica capillary column; temperature program with 30°C hold; and direct interface to mass spectrometer. The end of the capillary column is inserted as close as possible to the ion source of the mass spectrometer, however without intercepting the electron beam.

3.1.1 Column

Fused silica capillary column, 30 m x 0.25 mm ID, coated with 0.25 micron thickness of DB-5 bonded phase silicone. (J&W Scientific DB-5-30N, or equivalent).

3.1.2 Carrier Gas Supply

Hydrogen or helium can be used as carrier gases. If hydrogen is employed, safe handling practices must be used.

Hydrogen and helium must be oxygen-free. Ultrapure helium (99.999 percent) can be used directly from the cylinder, however, it is desirable to install a de-oxo cartridge to remove residual oxygen in case of leaks.

3.2 Mass Spectrometer

A mass spectrometer with electron impact ion source is required. The mass spectrometer should be interfaced with the gas chromatograph via a heated capillary transfer line. The mass spectrometer should be interfaced to a data system that allows acquisition and storage of repetitive scan data throughout the GC/MS run.

3.3 Computer and Programs

A computer system that allows searching of the GC/MS data for display of extracted ion current profiles and integration of peak areas is required. Furthermore, the capability to generate response factors from the analysis of standards to accumulate calibration data to standardize system performance and assure reproducible results is desirable. If this capability is not available, these data must be produced manually for every calibration compound analyzed to permit an updating of response factors to meet the specifications of the protocol.

4. COLUMN INSTALLATION AND FLOW ADJUSTMENT

4.1 Column Installation

4.1.1 Slide fitting nuts and ferrules onto each end of the column, (Vespel ferrules treated with graphite are recommended). Cut 2 to 3 cm from each end of the column by scoring the circumference with a sharp edged file or razor blade, and break off the column ends with the fingers.

4.1.2 Insert one end of the column into the injection port to a position 0.5 to 2.0 cm from the tip of a fully inserted syringe needle. Tighten the nut finger tight, then turn it one full turn with a wrench.

4.1.3 Insert the outlet end of the column into the ion source and position it. Tighten the nut finger tight, then turn it one full turn with a wrench.

4.1.4 Leak test the column inlet and outlet fittings with argon using the mass spectrometer as a leak detector.

4.1.5 Position the column inside the oven such that any contact between the oven wall and the column is avoided.

4.2 Flow Adjustment

4.2.1 Set the column head pressure at 10 psig and the oven temperature to 30°C.

4.2.2 Measure the linear gas velocity by injecting a small quantity of air and recording the transit time through the column using the mass spectrometer as the detector for air (at m/e 28).

4.2.3 Adjust the column head pressure until the linear gas velocity is 40-60 cm per second at 30°C column temperature if hydrogen is used as the carrier gas. If helium is used as the carrier gas the desired flow is 25 to 30 cm per second. For wider bore columns the gas flow is determined by the vacuum system. Typical linear gas velocities for wider bore columns (0.32 mm ID) are 60 to 80 cm per second for hydrogen and 30 to 40 cm per second for helium.

5. OPERATING CONDITIONS

5.1 Split/Splitless Injector

Dimensions: 2 to 3 mm ID
Material: Quartz or glass
Temperature: 280°C
Flow rates:

Sweep flow: 10 mL/min
Split flow: 35 mL/min
Stop flow for 0.5 min at start of program

5.2 Column Temperature Program

Initial temperature: 30°C
Initial hold: 4 min
Rate: 8°C/min
Final temperature: 300°C
Final hold: 10 min

5.3 Mass Spectrometer

Mass range: m/e 40-450
Scan time: 0.75 ± 0.25 second
Electron energy: 70 eV
Source temperature: 280 to 300°C
initiate acquisition of data with start of GC program

6. SAMPLE PREPARATION

6.1 Analytical Standards

Prepare mixed analytical standards from commercially available stock standards that are certified by the manufacturer or an independent source. The purity of the compounds in the original stock standards should be noted; if greater than 98 percent no correction is needed estimate the concentration of the specified analyte. Working solutions containing the compounds of interest at the three levels, 20, 500, and 200 micrograms per milliliter, should be prepared by diluting aliquots of the original stock solutions. All analytical standards should contain the internal standards and system performance standards at concentrations of 50 micrograms per milliliter.

6.2 Internal Standards

The internal standards (I.S.) which have been used successfully are bromobenzene-d_5, naphthalene-d_8, biphenyl-d_{10}, acenaphthene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, chrysene-d_{12}, and benzo(a)pyrene-d_{12}. Other I.S. may also be employed, however, the considerations given in Reference 1 must be addressed. A solution of the eight I.S. is prepared in methylene chloride-benzene (9:1) at a concentration of 1.0 milligram per milliliter each.

Each I.S. is spiked into each sample at 50 micrograms per milliliter. for complex samples higher levels of I.S. (e.g., 100 micrograms per milliliter) may be utilized to facilitate detection and identification, but care must be taken to avoid saturation.

6.3 System Performance Standards

The standards which have been used successfully to evaluate column performance are phenol-d_5, aniline-d_5, nitrobenzene-d_5, and 2,4-dinitrophenol-d_3. Decafluorotriphenylphosphine (DFTPP) is used to check the mass spectrometer tuning. These standards are added to the internal standard mixture and spiked into each sample at the same concentration as the internal standards. The system performance standards are also employed as quantification internal standards with respect to the unlabeled counterparts.

7. SAMPLE INJECTION

For the split/splitless technique, the flows are turned off for 0.5 minute, and at 0.1 minute a one-microliter sample is injected quickly. The needle is removed immediately. Thorough rinsing of the syringe following sample injection is required.

The performance of the splitless injection is the most critical step in the procedure. Poor injections lead to discrimination of either the low or the high boiling compounds and consequently to poor analytical precision. A correct injection technique should give reproducible response factors for each I.S. relative to phenanthrene-d_{10}.

8. QUALITATIVE AND QUANTITATIVE IDENTIFICATION

8.1 Relative Retention Time Criteria

The use of eight I.S. allows for the accurate measurement of relative retention times (RRT) for all compounds. The values in Table Q-1 were obtained with new columns under the conditions noted. As columns are shortened or are modified by the injected components the RRTs change. Variation in columns, oven temperatures and temperature programs can also have effects on RRTs. The RRTs should be very reproducible over several days. The identification criteria require that the retention time of a listed compound in a unknown agree within ±8 seconds of that in the daily standard.

8.2 Mass Spectral Criteria

All fragment ions with intensities greater than 10 percent of the base peak in the mass spectrum of the standard must be present in the mass spectrum of the compound in the sample. Relative abundances must agree within ±20 percent. Furthermore, the absolute abundance of all characteristic ions must co-maximize within ± one; i.e. three consecutive scans.

8.3 Determination of Relative Response Factors

8.3.1 Analyze the 20, 50, and 200 micrograms per milliliter standards as described in Section 9.3 at least once each week.

8.3.2 Calculate relative response factors of each compound in Table Q-1 using the appropriate internal standard as indicated in the table. The relative response factor (RRF) is defined as follows:

$$\text{RRF} = \frac{A_x}{A_{is}} \times \frac{W_{is}}{W_x}$$

where:

A_x = area counts of the quantification ion of compound X
A_{is} = area counts of the quantification ion of internal standard
W_x = amount of compound injected
W_{is} = amount of internal standard injected

For the purpose of reproducibility, all compounds must be quantified using the specific quantification ions listed in Table Q-1. These ions have been chosen to minimize interferences as well as to minimize mass differences from the internal standard. If serious interference occurs at the primary quantification ion, a secondary ion may be used as described in Method 625.(2)

TABLE Q-1r. RETENTION AND RESPONSE DATA FOR SEMIVOLATILE COMPOUNDS

No.	Compound	Quan Mass	RT (sec)	RRT(REF)	RF(REF)
4	*Bromobenzene-D5	82	639	1.000(4)	0.59(118)
1	4-Methylpyridine	93	540	0.840(4)	0.95(4)**
2	1,4-Dichlorobutane	55	608	0.951(4)	1.16(4)
3	Anisole	108	622	0.974(4)	1.06(4)
5	Bromobenzene	77	642	1.004(4)	1.04(4)
6	2,4-Dimethylpridine	107	643	1.007(4)	0.98(4)**
7	4-Chlorotoluene	126	681	1.066(4)	0.56(4)
8	2-Fluoroaniline	111	684	1.072(4)	1.35(4)
9	Benzaldehyde	106	685	1.074(4)	0.62(4)
10	Thiophenol	110	691	1.082(4)	0.16(4)
11	Pentachloroethane	119	707	1.107(4)	0.35(4)
12	Aniline-D5	98	708	1.109(4)	0.84(118)
13	Aniline	93	710	1.113(4)	1.09(12)
14	Phenol-D5	99	712	1.117(4)	0.76(118)
15	Phenol	94	714	1.121(4)	0.92(14)
16	Bis(2-chloroethyl) ether	93	723	1.134(4)	1.10(4)
17	2-Chlorophenol	128	272	1.141(4)	0.99(4)
18	Pentafluorophenol	184	729	1.145(4)	0.29(4)
19	1,2,4-Trimethylbenzene	105	733	1.150(4)	1.82(4)
20	2,4,6-Trimethylpyridine	121	754	1.186(4)	0.89(4)**
21	1,4-Dichlorobenzene	146	758	1.186(4)	1.32(4)
22	Benzyl chloride	91	760	1.190(48)	1.90(4)
48	*Naphthalene-D8	136	977	1.000(48)	1.39(118)
23	Benzyl alcohol	108	787	0.805(48)	0.29(48)
24	1,2-Dichlorobenzene	146	789	0.897(48)	0.31(48)
25	2-Methylphenol	108	812	0.831(48)	0.34(48)
26	N-Methylaniline	106	829	0.848(48)	0.65(48)
27	Acetophenone	105	831	0.850(48)	0.50(31)
28	4-Methylphenol	108	837	0.856(48)	0.36(48)
29	4-Methylaniline	107	838	0.857(48)	0.51(48)
30	Hexachloroethane	117	841	0.860(48)	0.16(48)
31	Nitrobenzene-D5	128	855	0.879(48)	0.24(118)
32	Nitrobenzene	123	858	0.878(48)	1.03(31)
33	N,N-Dimethylaniline	120	862	0.882(48)	0.58(48)
34	4-t-Butylpyridine	120	874	0.895(48)	0.50(48)
35	1,2,4,5-Tetramethylbenzene	119	894	0.914(48)	0.72(48)
36	Decafluorobiphenyl	265	897	0.918(48)	0.11(48)

(continued)

TABLE Q-1r. (Continued)

No.	Compound	Quan Mass	RT (sec)	RRT(REF)	RF(REF)
37	4-Chlorobenzaldehyde	139	907	0.928(48)	0.21(48)
38	2-Nitrophenol	139	947	0.934(48)	0.19(48)
39	Benzal chloride	125	922	0.931(48)	0.43(48)
40	2,4-Dimethylphenol	122	928	0.950(48)	0.34(48)
41	2-Nitrotoluene	120	951	0.973(48)	0.24(48)
42	Tetralin	104	953	0.974(48)	0.53(48)
43	Propiophenone	105	955	0.976(48)	0.98(48)
44	2,6-Dimethylaniline	121	957	0.979(48)	0.40(48)
45	Benzoic acid	122	957	0.980(48)	0.17(48)**
46	2,6-Dichlorophenol	162	938	0.979(48)	0.30(48)
47	1,2,4-Trichlorobenzene	180	971	0.993(48)	0.32(48)
49	Naphthalene	128	981	1.003(48)	0.99(48)
50	4-Chlorophenol	128	985	1.009(48)	0.46(48)
51	4-Chloroaniline	127	997	1.021(48)	0.45(48)
52	2,4-Dichlorophenol	162	998	1.022(48)	0.30(48)
53	Hexachloropropene	213	1003	1.026(48)	0.18(48)
54	4-Nitrotoluene	137	1015	1.039(48)	0.21(48)
55	Hexachlorobutadiene	225	1007	1.041(48)	0.14(48)
56	Benzotrichloride	159	1025	1.054(48)	0.27(48)
57	1-Chloro-4-nitrobenzene	111	1042	1.072(48)	0.17(48)
58	Quinoline	129	1045	1.077(48)	0.70(48)
59	Bis(2-chloroethoxy) ethane	63	1079	1.117(48)	0.45(48)
87	*Acenaphthene-D10	164	1302	1.000(87)	0.74(118)
60	4-Chloro-3-methylphenol	142	1090	0.837(87)	0.45(87)
61	4-t-Butylphenol	135	1095	0.841(87)	1.15(87)
62	4-Bromoaniline	171	1104	0.848(87)	0.42(87)
63	2-Methylnaphthalene	142	1107	0.850(87)	1.21(87)
64	4-Chloro-2-methylaniline	141	1107	0.850(87)	0.37(87)
65	4-Chlorobenzoic acid	139	1141	0.876(87)	0.17(87)**
66	1,2,4,5-Tetrachlorobenzene	216	1145	0.879(87)	0.58(87)
67	2,4,6-Trichlorophenol	196	1165	0.895(87)	0.36(87)
68	2,4,5-Trichlorophenol	196	1172	0.900(87)	0.35(87)
69	Acetanilide	93	1192	0.016(87)	0.87(87)
70	Biphenyl-D10	164	1192	0.916(87)	1.53(118)
71	2-Chloronaphthalene	162	1195	0.918(87)	1.49(87)
72	Biphenyl	154	1196	0.019(87)	1.31(87)
73	1-Chloronaphthalene	162	1201	0.922(87)	0.93(87)

(continued)

TABLE Q-1r. (Continued)

No.	Compound	Quan Mass	RT (sec)	RRT(REF)	RF(REF)
74	4-Methylquinoline	143	1203	0.924(87)	0.81(87)
75	2-Ethylnaphthalene	141	1213	0.932(87)	1.15(87)
76	Phenyl ether	170	1218	0.935(87)	0.85(87)
77	2-Nitroaniline	138	1222	0.939(87)	0.36(87)
78	4-Bromobenzoic acid	200	1232	0.946(87)	0.10(87)**
79	3,4-Dichloroaniline	161	1246	0.957(87)	0.48(87)
80	2-Chloro-4-nitrophenol	173	1254	0.964(87)	0.15(87)
81	Acenaphthylene	152	1259	0.967(87)	0.63(87)
82	2,3-Dimethylnaphthalene	156	1260	0.967(87)	0.95(87)
83	1,3-Dinitrobenzene	168	1257	0.972(87)	0.25(87)
84	Dimethyl phthalate	163	1261	0.974(87)	1.30(87)
85	2,6-Dinitrotoluene	165	1278	0.981(87)	0.27(87)
86	3-Nitroaniline	138	1300	0.999(87)	0.31(87)
88	Acenaphthene	154	1307	1.004(87)	0.95(87)
89	2,4-Dinitrophenol-D3	187	1318	1.012(87)	0.05(118)
90	2,4-Di-t-butylphenol	191	1318	1.012(87)	1.36(87)
91	2,4-Dinitrophenol	184	1319	1.013(87)	1.00(89)
92	2-Naphthol	144	1323	1.016(87)	0.42(87)
93	2,6-Di-t-butyl-4-methylphenol	205	1325	1.017(87)	1.09(87)
94	Dibenzofuran	168	1338	1.027(87)	1.60(87)
95	4-Nitrophenol	109	1339	1.030(87)	0.13(87)
96	Pentachlorobenzene	250	1342	1.031(87)	0.44(87)
97	2,4-Dinitrotoluene	165	1349	1.036(87)	0.32(87)
98	1-Aminonaphthalene	143	1354	1.040(87)	0.77(87)
99	2,4,5-Trichloroaniline	195	1336	1.042(87)	0.42(87)
100	2,4-Dinitrochlorobenzene	202	1376	1.057(87)	0.12(87)
101	Fluorene	166	1402	1.076(87)	1.09(87)
102	4-Chlorophenyl phenyl ether	204	1405	1.079(87)	0.42(87)
103	4-Chloro-2-nitroaniline	172	1413	1.085(87)	0.24(87)
104	4-Nitroaniline	138	1416	1.087(87)	0.26(87)
105	2-Methyl-4,6-dinitrophenol	198	1423	1.093(87)	0.14(87)
118	*Phenanthrene-D10	188	1576	1.000(118)	1.00(118)
106	Diphenylamine	169	1430	0.907(118)	0.68(118)
107	Azobenzene	182	1435	0.910(118)	0.27(118)
108	Trifluralin	306	1474	0.935(118)	0.15(118)
109	2-Chloro-4-nitroaniline	172	1499	0.951(118)	0.13(118)

(continued)

TABLE Q-1r. (Continued)

No.	Compound	Quan Mass	RT (sec)	RRT(REF)	RF(REF)
110	4-Hydroxybiphenyl	170	1507	0.956(118)	0.70(118)
111	Hexachlorobenzene	284	1519	0.964(118)	0.23(118)
112	2,6-Dichloro-4-nitroaniline	206	1524	0.967(118)	0.09(118)
113	2,4-Dichlorophenoxyacetic acid	162	1535	0.974(118)	0.02(118)**
114	4-Aminobiphenyl	169	1546	0.981(118)	0.27(118)
115	Pentachlorophenol	266	1534	0.986(118)	0.11(118)
116	3,3'-Dichlorobiphenyl	222	1560	0.990(118)	0.40(118)
117	Pentachloronitrobenzene	237	1570	0.996(118)	0.07(118)**
119	Phenanthrene	178	1580	1.002(118)	1.00(118)
120	4,4'-Dichlorobiphenyl	222	1580	1.002(118)	0.42(118)
121	Anthracene	178	1588	1.008(118)	1.01(118)
122	Acridine	179	1597	1.013(118)	0.61(118)
123	Phenanthridine	179	1615	1.025(118)	0.67(118)
124	Carbazole	167	1621	1.028(118)	0.84(118)
125	Decafluorotriphenylphosphine	198	1659	1.052(118)	0.10(118)
126	2,4,5-Trichlorophenoxyacetic acid	196	1681	1.066(118)	0.01(118)**
134	Decafluorobiphenyl	212	1841	1.000(134)	0.94(118)
127	4-Chlorobenzaldehyde	149	1706	0.926(134)	1.59(134)
128	2-Nitrophenol	183	1715	0.931(134)	0.11(134)
129	Benzal chloride	292	1716	0.932(134)	0.23(134)
130	Anthraquinone	208	1732	0.940(134)	0.29(134)
131	Fluoranthene	202	1803	0.979(134)	0.98(134)
132	2,2',4,4',6,6'-Hexachlorobiphenyl	360	1824	0.991(134)	0.17(134)
133	2-Methylanthraquinone	222	1834	0.996(134)	0.25(134)
135	Pyrene	202	1844	1.001(134)	0.97(134)
143	*Chrysene-D12	240	2074	1.000(143)	0.64(118)
136	4,4'-DDE	246	1879	0.905(143)	0.31(143)
137	4,4'-DDD	235	1940	0.935(143)	0.47(143)**
138	Diethylstilbestrol	268	1979	0.954(143)	0.08(143)
139	4,4'-DDT	235	1995	0.961(143)	0.35(143)
140	Triphenyl phosphate	326	2020	0.974(143)	0.20(143)
141	Benzo(a)anthracene	228	2071	0.998(143)	1.00(143)
142	Methoxychlor	227	2073	0.999(143)	0.68(143)
144	3,3'-Dichlorobenzidine	252	2074	1.000(143)	0.18(143)
145	Chrysene	228	2079	1.002(143)	1.00(143)
146	Bis(2-ethylhexyl) phthalate	149	2100	1.012(143)	1.00(143)
150	*Benzo(a)pyrene-D12	264	2318	1.000(150)	0.52(118)

(continued)

TABLE Q-1r. (Continued)

No.	Compound	Quan Mass	RT (sec)	RRT(REF)	RF(REF)
147	Tri-(tolyl) phosphate	368	2222	0.958(150)	0.20(150)
148	Bis(2-ethylhexyl) sebacate	185	2243	0.967(150)	0.55(150)
149	Benzo(k)fluoranthene	252	2266	0.977(150)	1.05(150)
151	Hexachlorophene	196	2319	1.000(150)	0.03(150)**
152	Benzo(a)pyrene	252	2323	1.002(150)	0.99(150)
153	Dibenzocarbazole	267	2521	1.099(150)	0.54(150)
154	Indeno(1,2,3-cd)pyrene	276	2571	1.124(150)	0.80(150)
155	Dibenzo(a,h)anthracene	278	2568	1.127(150)	0.60(150)
156	Benzo(g,h,i)perylene	276	2639	1.157(150)	0.70(150)

*Compounds used as internal standards.
**Compounds which may give poor responses.

8.3.3 Calculate the relative response factors of each of the eight internal standards, except phenanthrene-d_{10}, and each of the four column performance standards using phenanthrene-d_{10} as the internal standard.

8.3.4 From the weekly three level standards data (20, 50, 200 ng injected) calculate the correlation coefficients of the area ratio, A_i/A_{is}, for each of the counterparts of the eight labeled internal standards. A correlation coefficient of at least 0.9990 for each of the eight compounds ensures that the dynamic range of the method is being achieved.

9. INITIAL VERIFICATION

9.1 Ion Abundance Calibration

Prior to any sample analyses it is necessary to establish standard mass spectral abundance criteria through the analysis of decafluorotriphenylphosphine (DFTPP). The ion abundance criteria of Method 625 (see Table Q-2) must be met for the analysis of 50 nanograms of DFTPP introduced via the GC. Compliance with these requirements may be determined by examination of the DFTPP spectrum obtained from a daily calibration check standard.

TABLE Q-2. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of mass 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	greater than 1% of mass 198
441	present but less than mass 443
442	greater than 40% of mass 198
443	17-23% of mass 442

9.2 System Sensitivity and Chromatographic Performance

The desired analytical range for an FSCC GC/MS method is 5 to 500 nanograms injected. It is difficult to determine amounts within this range for all compounds because of the large variation in the response factors of the extractable semivolatile compound. It is critical to set the system sensitivity so that the highest level (500 ng) of high-response compounds (such as naphthalene, dimethyl phthalate, and phenanthene) is slightly saturated. Experience with fused silica columns has shown that control of the peak area of phenanthrene-d_{10} is an adequate method for controlling the sensitivity and dynamic range of the method.

Prior to starting the weekly multilevel calibration procedure, the overall system sensitivity should be set by injecting phenanthrene alone or in a mixture. The instrument sensitivity can vary as a function of multiplier, column, injector and source interface characteristics. The optimum electron multiplier setting is that setting which will yield approximately 50 X the detection limit but less than one-fourth of the value where serious saturation occurs for 50 nanograms of phenanthrene. This value must be determined by experience for each instrument and instrumental configuration. (For a Finnigan 4000 with an INCOS data system an appropriate sensitivity setting has been found to give 50,000 to 125,000 area counts for 50 nanograms of phenanthrene or phenanthrene-d_{10}).

The chromatographic performance is checked by the on-column injection of fifty nanograms each of 2,6-dichloro-4-nitroaniline and pentachlorophenol. This check can be done concurrently with the tuning and sensitivity checks, or with the calibration check analysis (see Section 9.3). The 2,6-dichloro-4-nitroaniline and pentachlorophenol must both have response factors relative to phenanthrene-d_{10} of greater than 0.05.

9.3 Multilevel Calibration

Analyze mixed standards which contain 20, 50, and 200 µg/mL of the compounds of interest. The standards should also contain the surrogate spiking compounds at the same levels. Spike each calibration standard with all of the labeled internal standards and column performance standards. Inject 1 µL of each standard and acquire a complete run. Process the data for each compound at the three concentration levels. The following criteria must be met:

- The relative retention times of each compound in each run should agree to within 0.05 relative retention time units. Late eluting compounds usually will exhibit better agreement.
- The relative response factors should not fall below 50 percent of those given in Table Q-1.
- All compounds in Table Q-1 except those whose response factors are starred must be detectable at the 20 nanogram level.
- Relative response factors of all compounds in Table Q-1 except those whose response factors are starred should have a relative standard deviation of <25 percent over the range tested.
- The correlation coefficient for the three-point curve of ion current ratio versus amount (i.e. A_x/A_{is} versus W_x) must be 0.999 for the labeled/unlabeled analyte pairs. This coefficient must be calculated and reported for the eight unlabeled analogs of the I.S. (bromobenzene, naphthalene, biphenyl, acenaphthene, phenanthrene, pyrene, chrysene, and benzo(a)pyrene).
- The relative response factors for the internal standards and the column performance standards using phenanthrene-d_{10} as the internal standard should not fall below 50 percent of those given in Table Q-1. These relative response factors can be used to assess the injector discriminaton and the acidity, basicity, and polarity of the GC column.
- The relative response factors for the unlabeled analogues of the eight internal standards, with correction for the purity of the

labeled compounds must be 1.0 ± 0.2 at each level, i.e. 20, 50, and 200 ng.

- The percent relative standard deviations for the relative ion abundances of m/e 51, 69, 127, 275, and 442 of DFTPP must each be less than 20 percent for all runs that follow the daily calibration check standards.

10. ONGOING QC ACTIVITIES

10.1 System Calibration

Samples may be analyzed upon successful completion of the initial QC activity. A calibration check analysis at the 50 µg/mL level must be run before the analysis of each set of up to eight samples. A three level calibration at 20, 50, and 200 µg/mL must be run at least once a week. The system must be restandardized whenever the specifications in 9.3 are not met and after any major system maintenance such as new column installation or source cleaning.

10.2 Run Verification

During or after each data acquisition, the presence of all eight I.S. must be verified. The area counts of each internal standard should be recorded for each standard and sample analyzed. The percent deviation of the integrated ion current for each internal standard in the samples run during any one week should remain within one standard deviation. The area counts for each internal standard relative to phenanthrene-d_{10} should not vary by more than a factor of two from the value obtained in the most recent standard analysis. Failure to meet this criterion will require minor system maintenance. Breaking off one foot of the column or cleaning the injector sleeve will often improve sensitivity for the late eluting compounds; repositioning the front end of the column will often improve front-end performance. Poor injection technique can also lead to variable I.S. ratios.

Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration (Section 9.3) requires that the system should not be saturated for high response compounds at 200 micrograms per milliliter. An estimate of the safe upper limit for any compound can be obtained by dividing 200 by the response factor for that compound. For example, nitrobenzene, with a relative response factor of 0.25 can be reliably quantified to 200 divided by 0.25 or 800 micrograms per milliliter. If more than five compounds in any sample exceed the analytical range, that sample must be diluted, the internal standard concentration readjusted, and the sample reinjected.

10.3 Daily Calibration Check

The tuning of the instrument must be checked for each run by measuring the relative abundances of the DFTPP ions as described in Section 9.1. The chromatography and sensitivity checks must also be successfully completed (Section 9.2). The relative response factors and relative retention times obtained for each calibration check at 50 µg/mL must meet the specifications of Section 9.3.

If these criteria are met, then the RRF values for all compounds are added to the list of those obtained previously. The RRF values used for quantification are based on an average of the current daily calibration check standards and those obtained from the two previous calibration check runs providing the calibration check criteria are met. If the calibration check criteria are not met, major instrument repair may be needed. Prior to conducting major repairs make sure that the standard has not deteriorated or that the system is not saturated.

10.4 Special Cautions

Skill is required in using FSCC GC/MS routinely. Improper sample injection technique can lead to poor precision evidenced by volatility discrimination and component cross contamination. The use of improper solvents can lead to peak splitting for early eluting components. The sensitivity of the method is very dependent on the correct positioning of the front end of the column in the injector and the back end of the column in the ion source.

All laboratories using this protocol should be aware of the difficulties and have access to technical advice for troubleshooting.

11. DOCUMENTATION

The following QC documentation is required as support for the analytical data obtained using this protocol.

- GC/MS Run Log
  - A log of all GC/MS runs including the area counts and absolute retention times for phenanthrene-d_{10} must be reported using a form shown as Table R-1.
- Relative Ion Abundance Calibration
  - The relative ion abundances for DFTPP in each run must be tabulated using a form shown as Table R-2.
- Calibration Checks
  - All RRT and RRF data obtained from multilevel and single level calibration checks must be reported using forms shown as Tables R-3 and R-4.

TABLE R-1. GC/MS RUN LOG FOR SEMIVOLATILE COMPOUND ANALYSES

Laboratory ID __________

Run No.	Date	Run Identification	Area of D_{10}-Phen.	RT of D_{10}-Phen., seconds	Date of Sample Extn.
Avg.					
% RSD					

Form 15

TABLE R-2. RELATIVE ABUNDANCES OF DFTPP IONS IN SEMIVOLATILE COMPOUND ANALYSES

Laboratory ID ________

Run No.	Relative Abundance of Given Ion												
	51	68	69	70	127	197	198	199	275	365	441	442	443
Avg.													
% RSD													

Form 4S

TABLE R-3. RELATIVE RETENTION TIMES OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID__________

Compound	Relative Retention Times Obtained From GC-MS Calibration Run of Given Run Number																			Avg.	% RSD

Form 83

TABLE R-4. RESPONSE FACTORS OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID__________

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																		Avg.	% RSD

Form 98

- Chromatography Checks
  - All RT and RRF data obtained for the internal standards and column performance standards for each run must be tabulated using forms such as Tables R-5 and R-6.
  - Hard copies must be produced for the extracted ion current profiles for 2,6-dichloro-4-nitroaniline, (m/e 206) pentachlorophenol (m/e 266), and phenanthrene-d_{10} (m/e 188) from each calibration run at the 50 µg/mL level. These profiles should include the peak area counts shown in Figure 1.
- Data transcription is the responsibility of the participating laboratory and is subject to audit by Battelle and EMSL-LV.

12. References

1. Sauter, A. D., Betowski, L. D., Smith, T. R., Strickler, V. A., Beimer, B. G., Colby, B. N., and Wilkinson, J. E., "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants", J. High Resolut. Chromatogr. Chromatogr, Commun., 4, 366 (1981).
2. Eichelberger, J. W., Harris, L. E., and Budde, W. L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems", Anal. Chem., 47, 995 (1975).

TABLE R-5. RETENTION TIMES OF SEMIVOLATILE INTERNAL STANDARDS

Laboratory ID ________

Run No.	Retention Time of Given Internal Standard, seconds												
	BB	Anil	Phol	NB	Naph	Biph	Acen	DNP	Phen	DFTPP	Pyr	Chry	BaP
Avg.													
% RSD													

BB = D_5-Bromobenzene
Anil = D_5-Aniline
Phol = D_5-Phenol
NB = D_5-Nitrobenzene
Naph = D_8-Naphthalene

Biph = D_{10}-Biphenyl
Acen = D_{10}-Acenaphthene
DNP = D_3-2,4-Dinitrophenol
Phen = D_{10}-Phenanthrene
DFTPP = Decafluorotriphenylphosphine

Pyr = D_{10}-Pyrene
Chry = D_{12}-Chrysene
BaP = D_{12}-Benzo(a)pyrene

Form 55

TABLE R-6. RESPONSE FACTORS OF SEMIVOLATILE INTERNAL STANDARDS

Laboratory ID ___________

Run No.	Response Factor of Given Internal Standard												
	BS	Anil	Phol	NB	Naph	Biph	Acen	Phen	DNP	DFTPP	Pyr	Chry	BaP
Avg.													
% RSD													

BS = D_5-Bromobenzene
Anil = D_5-Aniline
Phol = D_5-Phenol
NB = D_5-Nitrobenzene
Naph = D_8-Naphthalene

Biph = D_{10}-Biphenyl
Acen = D_{10}-Acenaphthene
Phen = D_{10}- Phenanthrene
DNP = D_3-2,4-Dinitrophenol
DFTPP = Decafluorotriphenylphosphine

Pyr = D_{10}-Pyrene
Chry = D_{12}-Chrysene
BaP = D_{12}-Benzo(a)pyrene

Form 55

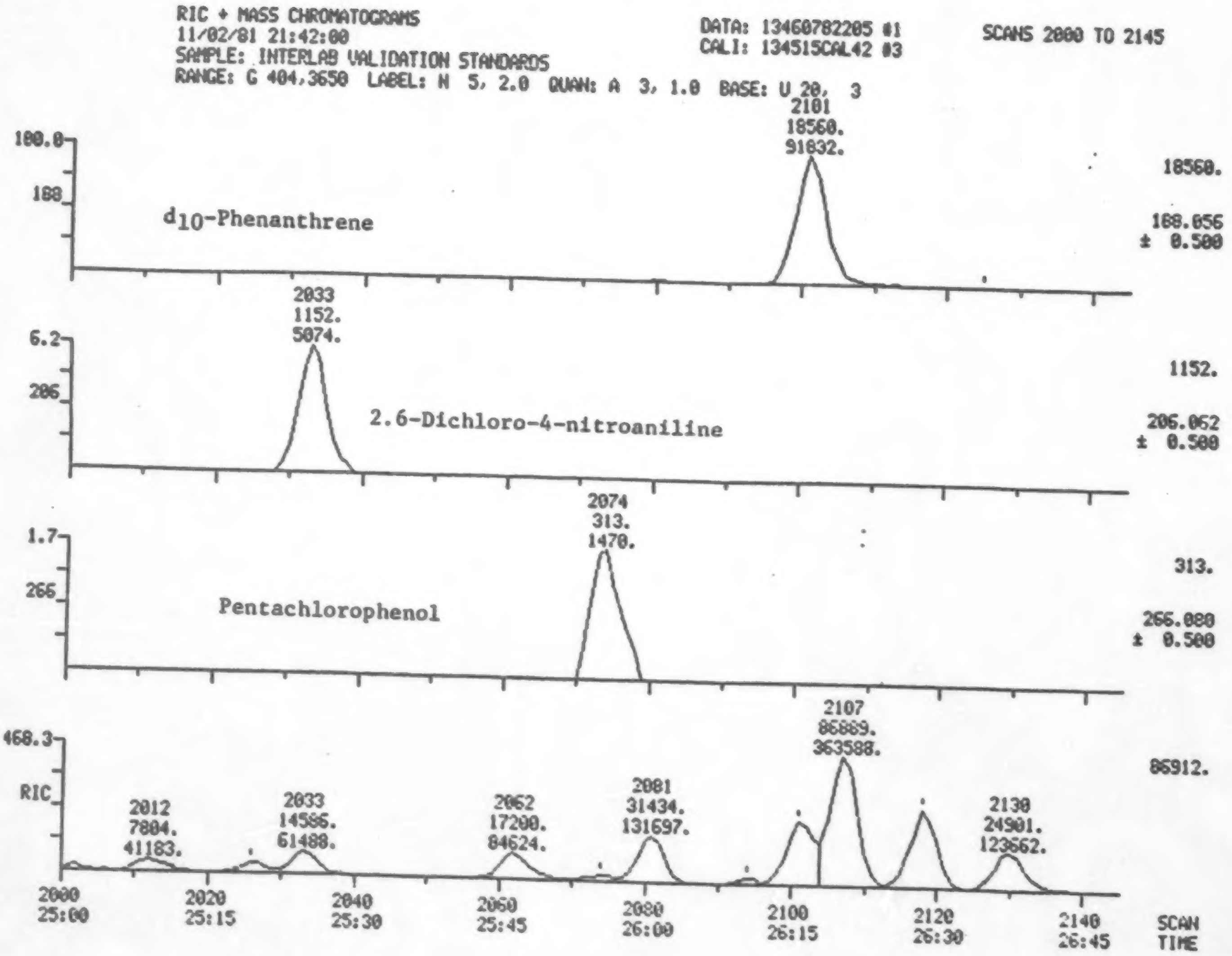


Figure 1. Chromatography/sensitivity check.

APPENDIX D

DESCRIPTION OF STANDARD SOLUTIONS

DESCRIPTION OF STANDARD SOLUTIONS

Semivolatile Calibration Solution A

(all compounds at 0.1 mg/mL in methylene chloride)

Aromatic Halocarbons

3,3'-Dichlorobiphenyl
4,4'-Dichlorobiphenyl
2,2'-4,4'-Tetrachlorobiphenyl
2,2'-4,4',6,6'-Hexachlorobiphenyl

Aromatic Hydrocarbons

Benzo(a)anthracene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Chrysene
Dibenzo(a,h)anthracene
Benzo(a)pyrene

Amines

1,2,7,8-Dibenzocarbazole

Semivolatile Calibration solution B

(all compounds at 1.0 mg/mL in benzene)

Aromatic Hydrocarbons

Naphthalene
1,2,4-Trimethylbenzene
1,2,4,5-Tetramethylbenzene
Biphenyl
Acenaphthylene
Acenaphthene
2-Methylnaphthalene
2-Ethylnaphthalene
2,3-Dimethylnaphthalene
1,2,3,4-Tetrahydronaphthalene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene

Amines

Aniline
4-Chloroaniline
4-Bromoaniline
2-Nitroaniline
3,4-Dichloroaniline
2,4,5-Trichloroaniline
3-Nitroaniline
4-Chloro-2-methylaniline
4-Nitroaniline
2,6-Dichloro-4-nitroaniline
2-Chloro-4-nitroaniline
2,4-Dinitroaniline
N-Methylaniline
4-Chloro-2-nitroaniline
4-Methylaniline
2,6-Dimethylaniline
4-Aminobiphenyl
1-Aminonaphthalene
N,N-Dimethylaniline
Phenanthridine
4-Methylpyridine
2,4-Dimethylpyridine
4-t-Butylpyridine
2,4,6-Trimethylpridine
Quinoline
4-Methylquinoline
Acridine
Carbazole
3,3'-Dichlorobenzidine
Diphenylamine

(continued)

Semivolatile Calibration Solution C
(all compounds at 0.5 mg/mL in methylene chloride)

Aliphatic Halocarbons

1,4-Dichlorobutane
Pentachloroethane
Hexachloroethane
Hexachloropropene
Hexachlorobutadiene

Aromatic Halocarbons

4-Chlorotoluene
Bromobenzene
1,2-Dichlorobenzene
1,4-Dichlorobenzene
1,2,4-Trichlorobenzene
1,2,4,5-Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene
Benzal chloride
Benzyl chloride
1-Chloronaphthalene
2-Chloronaphthalene
α,α,α-Trichlorotoluene

Aromatic Nitro Compounds

Nitrobenzene
1,3-Dinitrobenzene
2-Nitrotoluene
4-Nitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1-Chloro-4-nitrobenzene
2,4-Dinitrochlorobenzene

Phenols

2-Chlorophenol
2-Nitrophenol
Phenol
2,4-Dimethylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
4-Chloro-3-methylphenol
2-Methylphenol
4-Methylphenol
Thiophenol
4-Chlorophenol
2,6-Dichlorophenol
2,4,5-Trichlorophenol
Hexachlorophene
4-Hydroxybiphenyl
2-Naphthol
4-t-Butylphenol
2-Chloro-4-nitrophenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
Pentachlorophenol
4-Nitrophenol
2,6-Di-t-butyl-4-methylphenol
2,4-Di-t-butylphenol
Diethylstilbestrol

Chlorinated Pesticides

4,4'-DDD
4,4'-DDE
4,4'-DDT
Methoxychlor
Trifluralin
Pentachloronitrobenzene

Acids

4-Chlorobenzoic acid
Benzoic acid
4-Bromobenzoic acid
2,4-Dichlorophenoxyacetic acid
2,4,5-Trichlorophenoxyacetic acid

Haloethers

Bis(2-chloroethyl)ether
Bis(2-chloroethoxy)ethane
4-Chlorophenyl phenyl ether

(continued)

DESCRIPTION OF STANDARD SOLUTIONS (Continued)

Semivolatile Calibration Solution D
(all compounds at 1.0 mg/mL in methylene chloride)

Phthalates

Dimethyl phthalate
Di-n-butyl phthalate
Di(2-ethylhexyl) phthalate

Phosphates

Tri(p-tolyl) phosphate
Triphenyl phosphate

Aldehydes

Benzaldehyde
4-Chlorobenzaldehyde

Ethers and Sulfides

Anisole
Phenyl ether
Dibenzofuran

Ketones

Anthraquinone
2-Methylanthraquinone
Propiophenone
Acetophenone

Miscellaneous

Azobenzene
Acetanilide
Benzyl alcohol
Di(2-ethylhexyl) sebacate

Semivolatile Surrogate Standard Solution E
(all compounds at 10 mg/mL in methylene chloride)

Decafluorobiphenyl
2-Fluoroaniline
Pentafluorophenol

Semivolatile Internal Standard Solution F
(all compounds at 200 μg/mL in methylene chloride)

D_5-Bromobenzene
D_8-Naphthalene
D_{10}-Phenanthrene
D_{10}-Biphenyl
D_{10}-Acenaphthene
D_{10}-Pyrene
D_{12}-Chrysene
D_{12}-Benzo(a)pyrene
D_5-Aniline
D_5-Phenol
D_5-Nitrobenzene
D_3-2,4-Dinitrophenol
Decafluorotriphenylphosphine

(continued)

DESCRIPTION OF STANDARD SOLUTIONS (Continued)

Volatile Calibration Solution G
(all compounds at 0.2 mg/mL in methanol)

2-Chloroethylvinyl ether
1,1,2-Trichlorotrifluoroethane
Dibromomethane
Allyl chloride
Ethylene dibromide
Chloropicrin
2-Chloropropane
1-Chlorobutane
o-Xylene
Styrene
2-Butanone
Cyclopentanone
4-Methyl-2-pentanone
2-Hexanone
Carbon disulfide
Dimethyl disulfide
Epichlorohydrin
2-Chloroacrylonitrile
Acetonitrile
Dichloroacetonitrile
n-Propionitrile
Chloroacetaldehyde
2-Chloroethanol
N-Nitrosodimethylamine
Vinyl acetate
Dimethyl sulfide
Diethylether
Acetone
Methyl chloroacetate
Methyl acrylate
Methyl methacrylate

Volatile Surrogate Standard solution H
(all compounds at 10 mg/mL in methanol)

1,2-Dibromotetrafluoroethane
Bis(perfluoroisopropyl) ketone
Fluorobenzene
m-Bromobenzotrifluoride

Volatile Internal Standard Solution I
(all compounds at 0.2 mg/mL in methanol)

D_4-1,2-Dichloroethane
D_6-Benzene
D_5-Ethylbenzene
4-Bromofluorobenzene

Volatile Calibration Solution J
(all compounds at 0.2 mg/mL in water)

Acrolein
Acrylonitrile

(continued)

DESCRIPTION OF STANDARD SOLUTIONS (Continued)

Volatile Calibration Solution K

2-Chloroethyl vinyl ether 0.2 mg/mL in tetraglyme

Supelco's Purgeable A
(all compounds at 0.2 mg/mL in methanol)

Methylene chloride
1,1-Dichloroethene
1,1-Dichloroethane
Chloroform
Carbon tetrachloride
1,2-Dichloropropane
Trichloroethylene
1,1,2-Trichloroethane
Dibromochloromethane
Tetrachloroethene
Chlorobenzene

Supelco's Purgeable B
(all compounds at 0.2 mg/mL in methanol)

trans-1,2-Dichloroethene
1,2-Dichloroethane
1,1,1-Trichloroethane
Bromodichloromethane
trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
Benzene
Bromoform
1,1,2,2-Tetrachloroethane
Toluene
Ethylbenzene

Supelco's Purgeable C
(all compounds at 0.2 mg/mL in methanol)

Chloromethane
Bromomethane
Vinyl chloride
Chloroethane

MR-137-82

APPENDIX E

MANUAL FOR COLLABORATORS

EVALUATION OF METHODS FOR ANALYSIS OF HAZARDOUS WASTES

Manual for Collaborators

- Instructions
- Analysis Methods
- Report Forms
- Program Review Inquiry

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PROJECT DESCRIPTION

This interlaboratory study is part of a program to select, modify and evaluate methods for determination of organic constituents in hazardous wastes. The methods to be examined include one for determination of semivolatile organic compounds (boiling above ca. 150°C) and one for volatile organic compounds (boiling up to ca. 150°C), and were selected from several methods for analysis of solid wastes. The methods were modified to be applicable to a variety of waste types and were evaluated in one laboratory for applicability, precision and accuracy. The methods are now to be evaluated via an interlaboratory study.

Study Objective

The objective of this study is to evaluate the methodologies in terms of the effects of different laboratories and different waste types on data quality. The study is designed to evaluate the analysis procedure only. Sampling, standard sources, standard preparation and spiking procedures have been conducted by Battelle to avoid effects resulting from these sources.

Outline of Study

The study is designed for 10 participating laboratories each to analyze in triplicate several waste samples. The analyses will be conducted for semivolatile and volatile organic compounds. The samples delivered to the participants will have been previously spiked with certain compounds. Each waste sample will be delivered in one or two septum-sealed screw-cap vials. The sample amounts will be ample for all analyses required. The data resulting from the participating laboratories will be analyzed at Battelle to determine repeatability, reproducibility and recovery all as a function of waste type and laboratory.

The generated data will include analytical performance data that will provide criteria for quality control parameters in future application of the methods. Information will be solicited through a Program Review Inquiry Form regarding any problems encountered in performing the methods and any recommendations for procedural change or procedure wording.

The program includes review of these instructions prior to use in laboratory work to ascertain that the instructions are understood. If changes result from the initial review, those changes will be incorporated in all instruction manuals before laboratory work begins.

Program Requirements

This package of instructions is identical to those sent to all participating laboratories and it is imperative that all work be peformed and all results be reported exactly as specified here.

It is expected that each participant has the apparatus for conducting the methods and has personnel that are competent in conducting analyses by GC/MS and analyses that depart from familiar procedures.

Participants are cautioned against making a number of repeated measurements and selecting the "best" ones or reporting an average of several measurements. Each laboratory must report each individual measurement as specified in the protocol. Runs for which known deviations from the protocol or accidents occur (spillage, evaporation to dryness, known contamination) should be aborted and rerun.

SUPPLIED ITEMS

The items supplied to each participating laboratory include:

- Instruction Manual
- Data Report Forms
- Performance Evaluation Samples
- Eight Waste Samples
- Fourteen Standard Solutions
  - -- 10 calibration standards
  - -- 2 internal standards
  - -- 2 surrogate standards
- 1 DB-5 Fused Silica Capillary Column
- GC/MS Data for 200 Organic Compounds
- GC/MS Library for INCOS Users

Any laboratory experiencing equipment or supply problems that might cause a delay in reporting data on time should contact Battelle program personnel immediately. Battelle will respond to questions in less than 24 hours. Any additional supplies that are needed and that can be provided by Battelle will be shipped within 24 hours of request.

Instruction Manual

This instruction manual was prepared to provide information necessary for the conduct of the study by each participant. All laboratory personnel to be associated with the program should become familiar with the manual prior to initiation of experimental work. This manual is to be accessible to all personnel during all phases of the study. Any ambiguities not resolved during the review of the manual are to be referred to Battelle by telephone and followed up by written communication. The Battelle personnel who are to be contacted include one of the following:

	Scott Warner	(614) 424-5643
	Dick Heffelfinger	(614) 424-5249
or	Mary McKown	(614) 424-5896

Address written communication to the Battelle person contacted at this address:

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Data Report Forms

Examples of the data report forms to be used for reporting the data specified as deliverables are contained in this instruction manual. An appropriate supply of each of the forms is provided in the accompanying packages.

Performance Evaluation Samples

The samples to be analyzed by each participating laboratory to demonstrate acceptable performance include:

1 prepared extract for semivolatile analysis (ILS-10)
1 prepared extract for volatile analysis (ILS-11)
1 solid waste sample (ILS-1) to be extracted and analyzed for
  -- semivolatile organics
  -- volatile organics

The methods to be employed are included in this instruction manual. During the two-week period allotted for analysis of the performance evaluation samples each laboratory will be visited by Battelle staff who will observe analysis techniques and answer any questions posed by participants.

Waste Samples

The solid waste samples were selected to represent a range of waste types that are commonly encountered and are distinctly different from each other. These samples have been spiked, homogenized, and divided into aliquots for distribution to participating laboratories. The waste samples and the performance evaluation samples are listed in Table 1.

The samples are to be analyzed for the 200 compounds listed in Table 2 and for as many as 20 other compounds for which a significant peak is observed. It may not be possible to identify and quantify every compound listed in Table 2 for each waste sample. However, any compound not identified should be reported as not detected. The methods for the determination of semivolatile and volatile organic compounds included in this instruction manual are to be followed for the extractions and analyses.

Calibration Standards

Fourteen solutions containing chemically compatible calibration standards are provided to serve as reference points that are identical for all of the participating laboratories. The solutions provided are labeled by letters A through I and contain the compounds listed in Table 3.

Fused Silica Capillary Column

To avoid delays in conducting this interlaboratory study Battelle purchased 10 DB-5 fused silica capillary columms from J&S Scientific Company. Each column was checked at Battelle and meets performance requirements. This column is the only column to be used for the semivolatile analyses and the column provided is not to be used for any other work before the interlaboratory study is completed.

TABLE 1. INVENTORY OF SUPPLIED WASTE SAMPLES

Battelle Number	Sample Identification	Description	Analysis to be Performed[a]
ILS-1	Contaminated soil	Wet solid	S, V
ILS-2	Latex paint waste	Aqueous dispersion	S, V
ILS-3	Ethanes spent catalyst	Oily powder	S, V
ILS-4	Coal gasification tar	Tar	S, V
ILS-5	Oxychlorination catalyst	Pelletized solid	S, V
ILS-6	Chemically treated POTW sludge	Wet solid	S, V
ILS-7	Herbicide acetone waste	Liquid	V
ILS-8	Chlorinated ethanes waste	Liquid	V
ILS-9	Contaminated sediment	Dry solid	S
ILS-10	Methylene chloride extract	Solution	S
ILS-11	Tetraglyme extract	Solution	V

(a) S - Semivolatile compounds
V - Volatile compounds

GC/MS Data

GC/MS Data collected by Battelle for the 200 compounds are provided in Table Q-1 from the Quality Control Protocol for Fused Silica Capillary Columns and Table 4. These data include:

- Response factors
- Retention time
- Relative retention time
- Quantification ion
- Internal standard to be used for quantification

The operating parammeters are specified in the methodology description.

TABLE 2. 200 COMPOUNDS TO BE DETERMINED IN SOLID WASTES

Purgeables

Purgeable Halocarbons

- Chloromethane
- Bromomethane
- Vinyl chloride
- Chloroethane
- Methylene chloride
- Ethyl bromide
- 1,1-Dichloroethene
- 1,1-Dichloroethane
- trans-1,2-Dichloroethene
- Chloroform
- 1,2-Dichloroethane
- 1,1,1-Trichloroethane
- Carbon tetrachloride
- Bromodichloromethane
- 1,2-Dichloropropane
- trans-1,3-Dichloropropene
- Trichloroethene
- Dibromochloromethane
- 1,1,2-Trichloroethane
- cis-1,3-Dichloropropene
- 2-Chloroethylvinyl ether
- Bromoform
- 1,1,2,2-Tetrachloroethane
- Terachloroethene
- Chlorobenzene
- 1,1,2-Trichlorotrifluoroethane
- Dibromomethane
- Allyl chloride
- Ethylene dibromide
- Chloropicrin
- 2-Chloropropane
- 1-Chlorobutane

Purgeable Hydrocarbons

- Benzene
- Toluene
- Ethylbenzene
- o-Xylene
- Styrene

Purgeable Oxygen, Sulfur, or Nitrogen Compounds

- 2-Butannone
- Cyclopentanone
- 4-Methyl-2-pentanone
- 2-Hexanone
- Carbon disulfide
- Dimethyl disulfide
- Acrylonitrile
- Epichlorohydrin
- 2-Chloroacrylonitrile
- Acetonitrile
- Dichloroacetonitrile
- n-Propionitrile
- Acrolein
- Chloroacetaldehyde
- 2-Chloroethanol
- N-Nitrosodimethylamine
- Vinyl acetate
- Dimethyl sulfide
- Diethyl ether
- Acetone
- Methyl chloroacetate
- Methyl acrylate
- Methyl methacrylate

Aliphatic Halocarbons

- 1,4-Dichlorobutane
- Pentachloroethane
- Hexachloroethane
- Hexachloropropene
- Hexachlorobutadiene

Aromatic Halocarbons

- 4-Chlorotoluene
- Bromobenzene
- 1,2-Dichlorobenzene
- 1,4-Dichlorobenzene
- 1,2,4-Trichlorobenzene
- 1,2,4,5-Tetrachlorobenzene

Semivolatiles

Aromatic Halocarbons

- Pentachlorobenzene
- Hexachlorobenzene
- 3,3'-Dichlorobiphenyl
- 4,4'-Dichlorobiphenyl
- 2,2',4,4'-Tetrachlorobiphenyl
- Benzal chloride
- 2,2',4,4',6,6'-Hexachlorobiphenyl
- Benzyl chloride
- 1-Chloronaphthalene
- 2-Chloronaphthalene
- α,α,α-Trichlorotoluene

Aromatic Hydrocarbons

- Naphthalene
- 1,2,4-Trimethylbenzene
- 1,2,4,5-Tetramethylbenzene
- Biphenyl
- Acenaphthylene
- Acenaphthene
- 2-Methylnaphthalene
- 2-Ethylnaphthalene
- 2,3-Dimethylnaphthalene
- 1,2,3,4-Tetrahydronaphthalene
- Fluorene
- Phenanthrene
- anthracene
- Fluoranthene
- Pyrene
- Benzo(a)anthracene
- Chrysene
- Benzo(k)fluorannthene
- Benzo(a)pyrene
- Dibenzo(a,h)anthracene
- Benzo(g,h,i)perylene
- Indeno(1,2,3-cd)pyrene

(continued)

TABLE 2. (Continued)

Semivolatiles

Aromatic Nitro Compounds

Nitrobenzene
1,3-Dinitrobenzene
2-Nitrotoluene
4-Nitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene

1-Chloro-4-nitrobenzene
2,4-Dinitrochlorobenzene

Phenols

2-Chlorophenol
2-Nitrophenol
Phenol
2,4-Dimethylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
4-Chloro-3-methylphenol
2-Methylphenol
4-Methylphenol
Thiophenol
4-Chlorophenol
2,6-Dichlorophenol
2,4,5-Trichlorophenol
Hexachlorophene
4- Hydroxybiphenyl
2-Naphthol
4-t-Butylphenol
2-Chloro-4-nitrophenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
Pentachlorophenol
4-Nitrophenol
2,6-Di-t-butyl-4-methylphenol
2,4-Di-t-butylphenol
Diethylstilbestrol

Amines

Aniline
4-Chloroaniline
4-Bromoaniline

Amines

2-Nitroaniline
3,4-Dichloroaniline
2,4,5-Trichloroaniline
3-Nitroaniline
4-Chloro-2-nitroaniline
4-Nitroaniline
2,6-Dichloro-4-nitroaniline
2-Chloro-4-nitroaniline
2,4-Dinitroaniline
N-Methylaniline
4-Chloro-o-2-methylaniline
4-Methylaniline
2,6-Dimethylaniline
4-Aminobiphenyl
1-Aminonaphthalene
N,N-Dimethylaniline
Phenanthridine
4-Methylpyridine
2,4-Dimethylpyridine
4-t-Butylpyridine
1,2,7,8-Dibenzocarbazole
2,4,6-Trimethylpyridine
Quinoline
4-Methylquinoline
Acridine
Carbazole
3,3-Dichlorobenzidine
Diphenylamine

Chlorinated Pesticides

4,4'-DDD
4,4'-DDE
4,4'-DDT
Methoxychlor
Trifluralin
Pentachloronitrobenzene

Phthalates

Dimethyl phthalate
Di-n-butyl phthalate
Di(2-ethylhexyl) phthalate

Phosphates

Tri(p-tolyl) phosphate
Triphenyl phosphate

Aldehydes

Benzaldehyde
4-Chlorobenzaldehyde

Ethers and Sulfides

Anisole
Phenyl ether
Dibenzofuran

Ketones

Anthraquinone
2-Methylanthraquinone
Propiophenone
Acetophenone
4-Chlorobenzoic acid
Benzoic acid
4-Bromobenzoic acid
2,4-Dichlorophenoxyacetic acid
2,4,5-Trichlorophenoxyacetic acid

Haloethers

Bis(2-chloroethyl)ether
Bis(2-chloroethoxy)ethane
4-Chlorophenyl phenyl ether

Miscellaneous

Azobenzene
Acetanilide
Benzyl alcohol
Di(2-ethylhexyl) sebacate

TABLE 3. DESCRIPTION OF STANDARD SOLUTIONS

Semivolatile Calibration Solution A
(all compounds at 0.1 mg/mL in methylene chloride)

Aromatic Halocarbons

3,3'-Dichlorobiphenyl
4,4'-Dichlorobiphenyl
2,2'-4,4'-Tetrachlorobiphenyl
2,2'-4,4',6,6'-Hexachlorobiphenyl

Aromatic Hydrocarbons

Benzo(a)anthracene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Chrysene
Benzo(a)pyrene
Dibenzo(a,h)anthracene

Amines

1,2,7,8-Dibenzocarbazole

Semivolatile Calibration Solution B
(all compounds at 1.0 mg/mL in benzene)

Aromatic Hydrocarbons

Naphthalene
1,2,4-Trimethylbenzene
1,2,4,5-Tetramethylbenzene
Biphenyl
Acenapththylene
Acenaphthene
2-Methylnaphthalene
2-Ethylnaphthalene
2,3-Dimethylnaphthalene
1,2,3,4-Tetrahydronaphthalene
Fluorene
Phenanthrene
Anthracene
Fluroanthene
Pyrene

Amines

Aniline
4-Chloroaniline
4-Bromoaniline
2-Nitroaniline
3,4-Dichloroaniline
2,4,5-Trichloroaniline
3-Nitroaniline
4-Chloro-2-methylaniline
4-Nitroaniline
2,6-Dichloro-4-nitroanilinne
2-Chloro-4-nitroaniline
2,4-Dinitroaniline
N-Methylaniline
2,6-Dimethylaniline
4-Aminobiphenyl
1-Aminonaphthalene
N,N-Dimethylaniline
Phenanthridine
4-Methylpyridinne
2,4-Dimethylpyridine
4-t-Butylpyridine
2,4,6-Trimethylpyridine
Quinoline
4-Methylquinoline
Acridine
Carbazole
3,3'-Dichlorobenzidine
Diphenylamine

(continued)

TABLE 3. (Continued)

Semivolatile Calibration Solution C
(all compounds at 0.5 mg/mL in methylene chloride)

Aliphatic Halocarbons

1,4-Dichlorobutane
Pentachloroethane
Hexachloroethane
Hexachloropropene
Hexachlorobutadiene

Aromatic Halocarbons

4-Chlorotoluene
Bromobenzene
1,2-Dichlorobenzene
1,4-Dichlorobenzene
1,2,4-Trichlorobenzene
1,2,4,5-Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene
Benzal chloride
Benzyl chloride
1-Chloronaphthalene
2-Chloronaphthalene
α,α,α-Trichlorotoluene

Aromatic Nitro Compounds

Nitrobenzene
1,3-Dinitrobenzene
2-Nitrotoluene
4-Nitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,-Chloro-4-nitrobenzene
2,4-Dinitrochlorobenzene

Phenols

2-Chlorophenol
2-Nitrophenol
Phenol
2,4-Dimethylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
4-Chloro-3-methylphenol
2-Methylphenol
4-Methylphenol
Thiophenol
4-Chlorophenol
2,6-Dichlorophenol
2,4,5-Trichlorophenol
Hexachlorophene
4-Hydroxybiphenyl
2-Naphthol
4-t-Butylphenol
2-Chloro-4-nitrophenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
Pentachlorophenol
4-Nitrophenol
2,,6-Di-t-butyl-4-methylphenol
2,4-Di-t-butylphenol
Diethylstilbestrol

Chlorinated Pesticides

4,4'-DDD
4,4'-DDE
4,4'-DDT
Methoxychlor
Trifluralin
Pentachloronitrobenzene

Acids

4-Chlorobenzoic acid
Benzoic acid
4-Bromobenzoic acid
2,4-Dichlorophenoxyacetic acid
2,4,5-Trichlorophenoxyacetic acid

Haloethers

Bis(2-chloroethyl)ether
Bis(2-chloroethoxy)ethane
4-Chlorophenyl phenyl ether

(continued)

TABLE 3. (Continued)

Semivolatile Calibration Solution D
(all compounds at 1.0 mg/mL in methylene chloride)

Phthalates

Dimethyl phthalate
Di-n-butyl phthalate
Di(2-ethylhexyl) phthalate

Phosphates

Tri(p-tolyl) phosphate
Triphenyl phosphate

Aldehydes

Benzaldehyde
4-Chlorobenzaldehyde

Ethers and Sulfides

Anisole
Phenyl ether
Dibenzofuran

Ketones

Anthraquinone
2-Methylanthraquinone
Propiophenone
Acetophenone

Miscellaneous

Azobenzene
Acetanilide
Benzyl alcohol
Di(2-ethylhexyl) sebacate

Semivolatile Surrogate Standard Solution E
(all compounds at 10 mg/mL in methylene chloride)

Decafluorobiphenyl
2-Fluoroaniline
Pentafluorophenol

Semivolatile Internal Standard Solution F
(all compounds at 200 µg/mL in methylene chloride)

D_5-Bromobenzene
D_8-Naphthalene
D_{10}-Phenanthrene
D_{10}-Biphenyl
D_{10}-Acenaphthene
D_{10}-Pyrene
D_{12}-Chrysene
D_{12}-Benzo(a)pyrene
D_5-Aniline
D_5-Phenol
D_5-Nitrobenzene
D_3-2,4-Dinitrophenol
Decafluorotriphenylphosphine

(continued)

TABLE 3. (Continued)

Volatile Calibration Solution G
(all compounds at 0.2 mg/mL in methanol)

2-Chloroethylvinyl ether
1,1,2-Trichlorotrifluoroethane
Dibromomethane
Allyl chloride
Ethylene dibromide
Chloropicrin
2-Chloropropane
1-Chlorobutane
o-Xylene
Styrene
2-Butanone
Cyclopentanone
4-Methyl-2-pentanone
2-Hexanone
Carbon disulfide
Dimethyl disulfide
Epichlorohydrin
2-Chloroacrylonitrile
Acetonitrile
Dichloroacetonitrile
n-Propionitrile
Chloroacetaldehyde
2-Chloroethanol
N-Nitrosodimethylamine
Vinyl acetate
Dimethyl sulfide
Diethylether
Acetone
Methyl chloroacetate
Methyl acrylate
Methyl methacrylate

Volatile Surrogate Standard solution H
(all compounds at 10 mg/mL in methanol)

1,2-Dibromotetrafluoroethane
Bis(perfluoroisopropyl) ketone
Fluorobenzene
m-Bromobenzotrifluoride

Volatile Internal Standard Solution I
(all compounds at 0.2 mg/mL in methanol)

D_4-1,2-Dichloroethane
D_6-Benzene
D_5-Ethylbenzene
4-Bromofluorobenzene

Volatile Calibration Solution J
(all compounds at 0.2 mg/mL in water)

Acrolein
Acrylonitrile

(continued)

TABLE 3. (Continued)

Volatile Calibration Solution K

2-Chloroethyl vinyl ether	0.2 mg/mL in tetraglyme

Supelco's Purgeable A
(all compounds at 0.2 mg/mL in methanol)

Methylene chloride
1,1-Dichloroethene
1,1-Dichloroethane
Chloroform
Carbon tetrachloride
1,2-Dichloropropane
Trichloroethylene
1,1,2-Trichloroethane
Dibromochloromethane
Tetrachloroethene
Chlorobenzene

Supelco's Purgeable B
(all compounds at 0.2 mg/mL in methanol)

trans-1,2-Dichloroethene
1,2-Dichloroethane
1,1,1-Trichloroethane
Bromodichloromethane
trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
Benzene
Bromoform
1,1,2,2-Tetrachloroethane
Toluene
Ethylbenzene

Supelco's Purgeable C
(all compounds at 0.2 mg/mL in methanol)

Chloromethane
Bromomethane
Vinyl chloride
Chloroethane

GC/MS Library

The GC/MS library developed by Battelle for the interlaboratory study is provided on 9-track tape to assist users with reverse search software. This library can be used only with the INCOS data systems. Hewlett-Packard users may prepare an equivalent library. Additional information required for the preparation of a library is given in Tables 5 and 6.

TABLE 4. CHARACTERISTIC MASSES AND INTENSITIES FOR SELECTED SEMIVOLATILE COMPOUNDS

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
4	*Bromobenzene-D5	82	52(20), 54(25), 82(100, 161(73), 163(70)
1	4-Methylpyridine	93	51(20), 65(25), 66(33), 67(15), 92(30), 93(100)
2	1,4-Dichlorobutane	55	41(20), 54(15), 55(100), 62(15), 90(22), 92(8)
3	Anisole	108	65(50), 77(15), 78(55), 79(15), 93(12), 108(100)
5	Bromobenzene	77	50(18), 51(20), 77(100), 156(76), 158(75)
6	2,4-Dimethylpyridine	107	65(20), 79(50), 92(20), 106(60), 107(100)
7	4-Chlorotoluene	126	62(11), 89(12), 91(100), 125(17), 126(40), 128(13)
8	2-Fluoroaniline	111	64(12), 83(17), 84(22), 91(10), 111(100)
9	Benzaldehyde	106	50(15), 51(30), 77(81), 78(12), 105(99), 106(100)
10	Thiophenol	110	66(30), 77(11), 84(18), 109(22), 110(100)
11	Pentachloroethane	119	117(06), 119(100), 121(30), 123(32), 130(32), 165(76), 167(95), 169(46)
12	Aniline-D5	98	70(10), 71(20), 97(10), 98(100)
13	Aniline	93	65(15), 66(32), 92(12), 93(100)
14	Phenol-D5	99	71(20), 99(100)
15	Phenol	94	65(14), 66(13), 94(100)
16	Bis(2-chloroethyl) ether	93	63(70), 65(25), 93(100), 95(30)
17	2-Chlorophenol	128	64(20), 100(20), 128(100), 130(30)
18	Pentafluorophenol	184	93(10), 117(35), 136(75), 137(10), 155(10), 184(100)
19	1,2,4-Trimethylbenzene	105	77(10), 91(10), 105(100), 119(12), 120(40)
20	2,4,6-Trimethylpyridine	121	77(11), 79(23), 106(15), 120(18), 121(100), 122(10)

(continued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
21	1,4-Dichlorobenzene	146	50(11), 74(13), 75(25), 111(40), 113(12), 146(100), 148(65), 159(10)
22	Benzyl chloride	91	65(13), 91(100), 92(81), 126(28), 128(8)
48	*Naphthalene-D8	136	108(11), 135(11), 136(100), 137(11)
23	Benzyl alcohol	108	51(20), 77(55), 78(12), 79(100), 91(15), 107(60), 108(90)
24	1,2-Dichlorobenzene	146	50(11), 74(12), 75(25), 111(40), 113(13), 146(100), 148(60), 150(10)
25	2-Methylphenol	108	27(28), 79(30), 80(13), 90(20), 107(80), 108(100)
26	N-Methylaniline	106	51(10), 77(25), 79(20), 106(100), 197(85)
27	Acetophenone	105	51(20), 77(65), 105(100), 120(25)
28	4-Methylphenol	108	77(23), 79(18), 90(8), 107(100), 108(90)
29	4-Methylaniline	107	77(15), 79(10), 106(100), 107(70)
30	Hexachloroethane	117	117(100), 119(95), 121(30), 164(40), 166(50), 199(53), 201(85), 203(55)
31	Nitrobenzene-D5	128	52(12), 54(45), 70(13), 82(100), 98(15), 128(60)
32	Nitrobenzene	123	50(12), 51(45), 65(13), 77(100), 93(15), 123(60)
33	N,N,-Dimethylaniline	120	77(22), 104(13), 105(13), 120(100), 121(90)
34	4-t-Butylpyridine	120	92(48), 120(100), 135(46)
35	1,2,4,5-Tetramethylbenzene	119	91(15), 119(100), 134(50)
36	Decafluorobiphenyl	265	167(12), 234(12), 265(40), 296(13), 315(13), 334(100), 335(13)
37	4-Chlorobenzaldehyde	139	50(20), 75(25), 111(60), 113(20), 139(100), 140(75), 141(40), 142(30)
38	2-Nitrophenol	139	53(13), 63(23), 64(18), 65(35), 81(23), 93(10), 109(25), 139(100)
39	Benzal chloride	125	63(13), 89(20), 125(100), 127(30), 160(10)

(continued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
40	2,4-Dimethylphenol	122	77(23), 79(13), 91(18), 107(06), 121(50), 122(100)
41	2-Nitrotoluene	120	63(14), 65(70), 77(16), 89(20), 91(45), 92(46), 120(100), 137(6)
42	Tetralin	104	78(10), 91(42), 104(100), 115(14), 117(15), 131(12), 132(5)
43	Propiophenone	105	51(13), 77(45), 105(100), 134(14)
44	2,6-Dimethylaniline	121	77(13), 91(12), 106(75), 120(60), 121(100), 122(10)
45	Benzoic acid	122	50(28), 51(48), 74(10), 77(78), 105(100), 122(80)
46	2,6-Dichlorophenol	162	63(42), 98(40), 99(15), 100(13), 126(18), 162(100), 164(63), 166(10)
47	1,2,4-Trichlorobenzene	180	74(20), 75(12), 109(22), 145(35), 147(20), 180(100), 182(98), 184(30)
49	Naphthalene	128	102(10), 127(13), 128(100), 129(12)
50	4-Chlorophenol	128	64(12), 65(30), 100(12), 128(100), 139(30)
51	4-Chloroaniline	127	63(10), 65(25), 92(20), 100(15), 127(100), 129(30)
52	2,4-Dichlorophenol	162	63(45), 98(30), 126(30)
53	Hexachloropropene	213	106(28), 117(32), 119(30), 141(38), 143(28), 211(63), 213(100), 215(67)
54	4-Nitrotoluene	137	63(15), 65(70), 77(15), 79(15), 89(15), 91(100), 107(30), 137(88)
55	Hexachlorobutadiene	225	118(37), 188(30), 190(47), 223(60), 225(100), 227(67), 260(36), 262(30)
56	Benzotrichloride	159	63(12), 89(18), 123(12), 159(100), 161(60), 163(10)
57	1-Chloro-4-nitrobenzene	111	50(30), 75(100), 99(38), 111(99), 113(30), 127(50), 157(85), 159(28)
58	Quinoline	129	51(97), 76(10), 102(28), 128(20), 129(100), 139(10)
59	Bis(2-chloroethoxy)ethane	63	45(20), 63(100), 65(35), 73(12), 93(63), 95(22), 197(33), 137(6)
70	*Biphenyl-D10	164	80(12), 82(10), 169(22), 164(100)

(continued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
60	4-Chloro-3-methylphenol	142	51(13), 77(40), 79(13), 197(100), 142(08), 144(30)
61	4-t-butylphenol	135	95(13), 107(35), 135(100), 136(11), 150(22)
62	4-Bromoaniline	171	92(80), 171(100), 173(80)
63	2-Methylnaphthalene	142	71(10), 115(20), 141(70), 142(100)
64	4-Chloro-2-methylaniline	141	77(25), 79(13), 106(100), 149(33), 141(80), 143(27)
65	4-Chlorobenzoic acid	139	75(20), 111(35), 113(15), 139(100), 141(30), 156(65), 158(20)
66	1,2,4,5-Tetrachlorobenzene	216	74(15), 108(15), 143(13), 180(20), 181(15), 214(76), 216(100), 218(46)
67	2,4,6-Trichlorophenol	196	97(53), 99(20), 132(50), 134(32), 160(23), 196(100), 198(99), 200(30)
68	2,4,5-Trichlorophenol	198	97(48), 99(18), 132(30), 133(18), 134(20), 196(98), 198(100), 200(30)
69	Acetanilide	93	43(12), 66(12), 93(100), 135(23)
71	2-Chloroanphthalene	162	126(18), 127(42), 162(100), 164(28)
72	Biphenyl	154	76(12), 152(23), 153(38), 154(100), 155(12)
73	1-Chloronaphthalene	162	126(18), 127(42), 162(100), 164(28)
74	4-Methylquinoline	143	89(10), 115(30), 142(20), 143(100), 144(10)
75	2-Ethylnaphthalene	141	115(20), 128(10), 141(100), 142(22), 156(50)
76	Phenyl ether	170	51(22), 77(30), 115(13), 141(50), 142(35), 169(25), 170(100), 171(12)
77	2-Nitroaniline	138	52(10), 65(63), 80(15), 92(50), 108(18), 138(100), 139(10)
78	4-Bromobenzoic acid	200	200(100), 202(98)
87	*Acenaphthene-D10	164	80(20), 82(11), 158(15), 160(35), 162(90), 163(20), 164(100), 165(13)
79	3,4-Dichloroaniline	161	63(14), 90(18), 99(18), 126(14), 161(100), 163(60), 165(10)

(connntinued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
80	2-Chloro-4-nitrophenol	173	63(45), 91(33),, 99(61), 107(33), 143(60), 145(20), 173(100), 175(33)
81	Acenaphthylene	152	63(78), 76(18), 150(15), 151(18), 152(100), 153(15)
82	2,3-Dimethylnaphthalene	156	115(20), 128(12), 141(90), 153(10), 155(23), 156(100), 157(12)
83	1,3-Dinitrobenzene	168	50(53), 64(23), 72(20), 74(82), 76(85), 92(50), 122(43), 168(100)
84	Dimethyl phthalate	163	50(11), 76(14), 77(18), 163(100), 164(10), 194(5)
85	2,6-Dinitrotoluene	165	63(36), 77(25), 89(40), 90(22), 121(18), 135(16), 148(23), 165(100)
86	3-Nitroaniline	138	65(82), 80(20), 92(92), 108(15), 138(100)
88	Acenaphthene	154	76(20), 77(11), 151(12), 152(45), 153(98), 154(100)
89	2,4-Dinitrophenol-D3	187	54(40), 66(37), 82(25), 94(30), 95(20), 110(35), 157(55), 187(100)
90	2,4-Di-t-butylphenol	191	57(18), 191(100), 192(13), 206(15)
91	2,4-Dinitrophenol	184	53(60), 63(76), 79(42), 91(58), 92(24), 107(44), 154(63), 184(100)
92	2-Naphthol	144	89(10), 115(70), 116(40), 144(100), 145(10)
93	2,6-Di-t-butyl-4-methylphenol	205	57(15), 145(72), 177(12), 205(100), 206(12), 220(28)
94	Dibenzofuran	168	140(33), 168(100), 169(12)
95	4-Nitrophenol	109	53(21), 63(18), 65(85), 81(20), 93(30), 109(30), 139(100), 140(10)
96	Pentachlorobenzene	250	108(23), 213(18), 215(23), 217(12), 248(60), 250(100), 252(70), 254(21)
97	2,4-Dinitrotoluene	165	63(28), 78(13), 89(50), 90(20), 119(26), 165(100), 182(5)
98	1-Aminonaphthalene	143	71(10), 115(35), 116(20), 143(100), 144(10)
99	2,4,5-Trichloroaniline	195	97(16), 124(20), 133(18), 135(12), 160(16), 195(100), 197(98), 198(30)
100	2,4-Dinitrochlorobenzene	202	63(38), 74(50), 75(92), 109(45), 110(60), 126(28), 202(100), 204(38)

(continued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
101	Fluorene	166	82(15), 83(13), 14(8), 163(15), 164(12), 165(88), 166(100), 167(13)
102	4-Chlorophenyl phenyl ether	204	51(18), 77(35), 115(12), 141(60), 169(15), 176(10), 204(100), 206(32)
103	4-Chloro-2-nitroaniline	172	63(32), 90(46), 99(48), 126(80), 128(26), 142(20), 172(100), 174(30)
104	4-Nitroaniline	138	64(10), 65(81), 80(15), 92(40), 108(45), 138(100)
105	2-Methyl-4,6-dinitrophenol	198	51(28), 77(17), 93(15), 105(40), 107(23), 121(35), 168(30), 198(100)
118	*Phenanthrene-D10	188	94(12), 160(1), 184(11), 187(13), 188(100), 189(13)
106	Diphenylamine	169	83(15), 167(30), 168(60), 169(100), 170(13)
107	Azobenzene	182	51(18), 77(100), 105(32), 152(10), 182(33)
108	Trifluralin	306	41(41), 43(100), 52(11), 145(10), 264(40), 290(15), 306(60), 335(2)
109	2-Chloro-4-nitroaniline	172	63(40), 90(93), 99(30), 126(32), 142(73), 144(22), 172(100), 174(32)
110	4-Hydroxybiphenyl	170	115(15), 141(20), 169(10), 179(100), 171(13)
111	Hexachlorobenzene	284	142(30), 214(18), 249(30), 251(20), 282(50), 284(100), 286(82), 288(35)
112	2,6-Dichloro-4-nitroaniline	206	124(98), 126(30), 160(50), 162(35), 176(85), 178(52), 206(100), 208(63)
113	2,4-Dichlorophenoxyacetic	162	133(30), 162(100), 168(68), 175(23), 220(65), 222(40)
114	4-Aminobiphenyl	169	115(8), 141(8), 167(10), 168(20), 169(100), 170(13)
115	Pentachlorophenol	266	165(40), 167(38), 202(15), 230(15), 264(68), 266(100), 268(65), 270(15)
116	3,3'-Dichlorobiphenyl	222	75(15), 93(11), 151(18), 152(70), 186(80), 222(100), 223(13), 224(65)
117	Pentachloronitrobenzene	237	142(62), 214(75), 235(66), 237(100), 239(68), 249(77), 293(68), 295(70)
119	Phenanthrene	178	89(12), 15(10), 176(18), 177(10), 178(100), 179(15)
120	4,4'-Dichlorobiphenyl	222	25(14), 93(11), 151(12), 152(70), 186(8), 222(100), 223(12), 224(64)

(continued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
121	Anthracene	178	89(12), 152(10), 176(18), 177(10), 178(100), 179(15)
122	Acridine	179	89(20), 151(10), 152(9), 178(23), 179(100), 180(15)
123	Phenanthridine	179	89(8), 151(15), 152(10), 178(23), 179(100), 180(15)
124	Carbazole	167	83(15), 139(11), 140(10), 166(18), 167(100), 168(12)
125	Decafluorotriphenylphosphine	198	69(60), 77(70), 127(60), 198(100), 255(40), 275(23), 442(50)
126	2,4,5-Trichlorophenoxyacetic	196	167(28), 196(100), 198(96), 200(30), 254(56), 256(50)
134	*Pyrene-D10	212	104(10), 106(15), 208(14), 211(12), 212(100), 213(15)
127	Di-n-butylphthalate	149	149(100), 150(10), 205(5), 223(5)
128	2,4-Dinitroaniline	183	52(35), 64(30), 91(58), 107(30), 153(65), 183(100)
129	2,2',4,4'-Tetrachlorobiphenyl	292	110(28), 150(30), 220(80), 222(50), 257(28), 290(73), 292(100), 294(48)
130	Anthraquinone	208	76(33), 150(18), 151(33), 152(77), 180(96), 207(17), 208(100), 209(16)
131	Fluoranthene	202	100(10), 101(18), 200(20), 201(15), 202(100), 203(18)
132	2,2',4,4',6,6'-Hexachlorobiphenyl	360	145(30), 218(30), 288(45), 290(60), 358(50), 360(100), 362(85), 364(30)
133	2-Methylanthraquinone	222	82(20), 165(05), 166(35), 194(50), 222(100)
135	Pyrene	202	100(11), 101(18), 200(18), 201(13), 202(100), 203(15)
136	4,4'-DDE	246	105(25), 176(40), 210(18), 246(100), 248(63), 316(43), 318(55), 320(28)
137	4,4'-DDD	235	165(50), 199(13), 235(100), 236(15), 237(63), 239(12)
138	Diethylstilbestrol	268	107(50), 145(53), 159(20), 224(13), 239(60), 253(13), 268(100), 269(20)
139	4,4'-DDT	235	165(40), 176(10), 199(12), 212(10), 235(100), 236(12), 237(65), 239(10)
140	Triphenylphosphate	326	65(37), 77(65), 169(37), 170(38), 215(38), 233(35), 327(99), 236(100)

(continued)

TABLE 4. (Continued)

No.	Compound	Quan Mass	Characteristic Ions (Intensity)
141	Benzo(a)anthracene	228	113(15), 114(20), 226(20), 228(100), 229(20)
142	Methoxychlor	227	113(10, 114(14), 120(13), 227(100), 228(15), 236(17)
143	*Chrysene-D12	240	118(12), 120(15), 236(22), 239(12), 240(100), 241(18)
144	3,3'-Dichlorobenzidine	252	91(16), 126(18), 127(16), 154(15), 182(9), 252(100), 254(65), 256(12)
145	Chrysene	228	113(12), 114(12), 226(28), 227(12), 228(100), 229(18)
146	Bis(2-ethylhexyl) phthalate	149	43(10), 57(20), 70(15), 71(18), 113(10), 149(100), 167(38), 279(9)
147	Tri-(p-tolyl) phosphate	368	107(35), 108(25), 165(30), 198(23), 261(23), 367(75), 368(100), 369(20)
148	Bis(2-ethylhexyl) sebacate	185	57(33), 70(23), 71(28), 83(13), 98(11), 112(20), 185(100), 186(11)
149	Benzo(k)fluoranthene	252	125(15), 126(20), 250(22), 252(100), 253(20)
150	*Benzo(a)pyrene-D12	264	12(13), 13(10), 13(21), 26(17), 26(100), 27(20)
151	Hexachlorophene	196	196(100), 198(98), 200(32), 208(43), 210(42), 404(18), 406(36), 408(29)
152	Benzo(a)pyrene	252	113(10), 125(12), 126(18), 250(20), 252(100), 253(20)
153	Dibenzocarbazole	267	132(16), 134(12), 256(12), 266(22), 267(100), 268(20)
154	Indeno(1,2,3-CD) pyrene	276	137(18), 138(30), 274(20), 275(11), 276(100), 277(23)
155	Dibenzo(a,h)anthracene	278	138(21), 139(34), 276(99), 277(15), 278(100), 279(25)
156	Benzo(g,h,i)Perylene	276	137(22), 138(30), 274(22), 275(11), 276(100), 277(23)

TABLE 5. RETENTION AND RESPONSE DATA FOR SELECTED VOLATILE COMPOUNDS

No.	Compound	Quan Mass	RT, sec.	RF(IS)
1	Chloromethane	50	200	2.422(21)
2	Bromomethane	94	320	2.502(21)
3	Vinyl chloride	62	386	2.063(21)
4	Chloroethane	64	472	2.388(21)
5	Methylene chloride	84	636	16.350(21)
6	Acetone	58	696	1.078(21)
7	Dimethyl sulfide	62	682	5.644(21)
8	Acrolein	56	692	2.422(21)
9	Bromoethane	108	688	6.695(21)
10	Acrylonitrile	53	734	2.422(21)
11	Carbon disulfide	76	738	14.626(21)
12	Propionitrile	55	798	0.206(21)
13	2-Chloropropane	78	782	1.082(21)
14	Allyl chloride	76	816	2.722(21)
15	1,1-Dichloroethylene	96	814	3.660(21)
16	trans-1,2-Dichloroethylene	96	930	4.136(21)
17	1,1-Dichloroethane	63	924	7.628(21)
18	Diethyl ether	59	954	5.549(21)
19	Chloroform	83	954	9.202(21)
20	1,1,2-Trichlorotrifluorethane	101	980	10.637(21)
21	*D_4-1,2-Dichloroethane	102	992	0.061(40)
22	2-Butanone	72	1000	1.850(21)
23	1,2-Dichloroethane	98	996	0.630(21)
24	Dibromomethane	93	1002	9.281(21)
25	1,2-Dibromotetrafluorethane	179	1016	4.916(21)
26	2-Chloroacrylonitrile	87	1032	7.636(21)
27	1,1,1-Trichloroethane	97	1072	7.265(21)
28	Carbon tetrachloride	117	1094	3.285(21)
29	Epichlorohydrin	57	1108	0.046(21)
30	Bromodichloromethane	127	1116	0.034(21)
31	Bis(perfluoroisopropyl)ketone	69	1124	0.211(21)
32	Methyl acrylate	55	1148	0.482(40)
33	Dichloroacetonitrile	74	1160	0.017(40)
34	Vinyl acetate	86	1178	0.014(40)
35	1-Chlorobutane	56	1182	0.774(40)

(continued)

TABLE 5. (Continued)

No.	Compound	Quan Mass	RT, sec.	RF(IS)
36	1,2-Dichloropropane	63	1200	0.340(40)
37	Dimethyl disulfide	94	1206	0.212(40)
38	trans-1,3-Dichloropropene	75	1212	0.377(40)
39	Trichloroethylene	130	1244	0.389(40)
40	*D_6-Benzene	84	1272	1.000(40)
41	Dibromochloromethane	127	1274	0.168(40)
42	1,1,2-Trichloroethane	97	1282	0.296(40)
43	cis-1,3-Dichloropropene	75	1286	0.305(40)
44	Benzene	78	1278	0.928(40)
45	Dibromomethane	107	1332	0.730(40)
46	Fluorobenzene	96	1354	0.923(40)
47	2-Chloroethylvinyl ether	63	1344	0.027(40)
48	Methyl methacrylate	100	1416	0.159(40)
49	Bromoform	173	1422	0.030(40)
50	4-Methyl-2-pentanone	58	1464	0.207(56)
51	2-Hexanone	58	1556	0.192(56)
52	1,1,2,2-Tetrachloroethane	83	1562	0.235(56)
53	Tetrachloroethylene	164	1572	0.211(56)
54	Toluene	92	1654	0.537(56)
55	Chlorobenzene	112	1720	0.600(56)
56	*D_5-Ethylbenzene	96	1822	1.116(40)
57	Ethylbenzene	91	1830	0.355(56)
58	*Bromofluorobenzene	174	1938	0.253(40)
59	Styrene	104	2006	1.118(56)
60	o-Xylene	106	2058	0.683(56)
61	m-Bromobenzotrifluoride	145	2182	0.303(56)

TABLE 6. CHARACTERISTIC MASSES AND INTENSITIES FOR SELECTED VOLATILE COMPOUNDS

No.	Compound	Quan Mass	Characteristic Ions, m/e (relative intensity)
1	Chloromethane	50	50(100), 52(33)
2	Bromomethane	94	94(100, 96(93)
3	Vinyl chloride	62	62(100), 64(33)
4	Chloroethane	64	64(100), 66(33)
5	Methylene chloride	84	49(100), 51(30), 84(55), 86(34)
6	Acetone	58	43(100), 58(35)
7	Dimethyl sulfide	62	47(100), 61(30), 62(80)
8	Acrolein	56	56(100), 55(70)
9	Bromoethane	108	108(100), 110(97)
10	Acrylonitrile	53	53(100), 52(80), 51(36)
11	Carbon disulfide	76	76(100), 78(10)
12	Propionitrile	55	55(100)
13	2-Chloropropane	78	63(100), 65(32), 78(81), 80(33)
14	Allyl chloride	76	76(100), 78(42)
15	1,1-Dichloroethylene	96	61(100), 96(54), 98(35)
16	trans-1,2-Dichloroethylene	96	61(100), 96(58), 98(37)
17	1,1-Dichloroethane	63	63(100), 65(32), 83(11), 85(7), 98(4) 100(3)
18	Diethyl ether	59	45(82), 59(100), 73(10), 74(100)
19	Chloroform	83	83(100), 85(65)
20	1,1,2-Trichlorotrifluorethane	101	85(44), 87(15), 101(100), 103(66), 153(53)
21	*D_4-1,2-Dichloroethane	102	51(35), 65(100), 67(55), 102(20), 104(12)
22	2-Butanone	72	43(100), 57(10), 72(20)
23	1,2-Dichloroethane	98	62(100), 64(32), 98(10), 100(6)
24	Dibromomethane	93	93(100), 95(80), 172(45), 174(85), 176(40)
25	1,2-Dibromotetrafluorethane	179	129(50), 131(50), 179(100), 181(98)
26	2-Chloroacrylonitrile	87	51(45), 52(100), 87(85), 89(28)
27	1,1,1-Trichloroethane	97	97(100), 99(63), 117(12), 119(11)
28	Carbon tetrachloride	117	117(100), 119(97), 121(32)
29	Epichlorohydrin	57	49(25), 51(8), 57(100)
30	Bromodichloromethane	127	83(100), 85(63), 127(7), 129(9)

(continued)

TABLE 6. (Continued)

No.	Compound	Quan Mass	Characteristic Ions, m/e (relative intensity)
31	Bis(perfluoroisopropyl)ketone	69	59(100), 69(60), 100(25), 169(20), 197(10)
32	Methyl acrylate	55	42(10), 55(100), 85(10)
33	Dichloroacetonitrile	74	74(100), 76(33), 82(55), 84(36)
34	Vinyl acetate	86	43(100), 86(10)
35	1-Chlorobutane	56	41(50), 43(30), 56(100)
36	1,2-Dichloropropane	63	62(70), 63(100), 65(31), 76(25)
37	Dimethyl disulfide	94	45(62), 46(38), 47(25), 79(60), 94(100)
38	trans-1,3-Dichloropropene	75	75(100), 77(27)
39	Trichloroethylene	130	95(100), 97(64), 130(97), 132(97)
40	*D_6-Benzene	84	56(12), 82(15), 84(100)
41	Dibromochloromethane	127	127(78), 129(100), 206(2), 208(5)
42	1,1,2-Trichloroethane	97	83(99), 85(63), 97(100), 99(63), 132(8), 134(8)
43	cis-1,3-Dichloropropene	75	75(100), 110(22), 112(18)
44	Benzene	78	78(100)
45	Dibromomethane	107	107(100), 109(98)
46	Fluorobenzene	96	50(10), 70(25), 75(8), 96(100)
47	2-Chloroethylvinyl ether	63	43(70), 44(50), 57(20), 63(100), 65(36), 106(20)
48	Methyl methacrylate	100	69(100), 100(46)
49	Bromoform	173	171(100), 173(100), 175(49), 250(2), 252(9), 254(8), 256(2),
50	4-Methyl-2-pentanone	58	57(58), 58(100), 85(33), 100(25)
51	2-Hexanone	58	57(30), 58(100), 100(12)
52	1,1,2,2-Tetrachloroethane	83	83(100), 85(66), 95(10)
53	Tetrachloroethylene	164	129(100), 131(62), 164(78), 166(100)
54	Toluene	92	91(100), 92(64)
55	Chlorobenzene	112	112(100), 114(32)

TABLE 6. (Continued)

No.	Compound	Quan Mass	Characteristic Ions, m/e (relative intensity)
56	*D_5-Ethylbenzene	96	96(100), 111(35)
57	Ethylbenzene	91	91(100), 106(31)
58	*Bromofluorobenzene	174	75(45), 95(100), 174(50), 176(49)
59	Styrene	104	77(12), 78(20), 103(32), 104(100)
60	o-Xylene	106	77(10), 91(100), 105(30), 106(60)
61	m-Bromobenzotrifluoride	145	75(30), 145(100), 224(61), 226(60)

*An internal standard.

QUALITY ASSURANCE/QUALITY CONTROL

The objective of Quality Assurance (QA)/Quality Control (QC) activities conducted for any chemical analysis program is to provide data of known quality. If the results of analyses are contested in any way, the quality of these data must be demonstrable.

While the data from this study are not likely to be directly contested in a pollution assessment case, the validity of the method may be contested and does need to be substantiated. The results of the study will form the basis for quality control requirements when the method is applied routinely.

QA Objectives

The objectives of QA/QC activities on this program are to make certain that the laboratory work conducted to evaluate the chemical analysis methods is done under controlled conditions, that those controls are uniformly applied by all collaborators and that all experimental work is recorded for archival storage.

In addition, when the analysis method is fully evaluated and is applied for routine analyses of hazardous wastes, the method description will include the necessary and appropriate quality control elements and requirements. Part of the requirements for that quality assurance and quality control will be based on experience and knowledge derived from this evaluation. Therefore, it is expected that all persons involved in this program will be aware of the ulimate use of the methods and will be alert, sensitive and critical to controls instituted to provide high quality data.

Documentation and Records

The documents for this program include the Manual of Instructions for collaborators of which this QA/QC plan is a part, the Program Review Inquiry form, data reports, letters of transmittal, records of telephone conversations relative to this program and all data and records associated with effort on this program. Copies of these documents will be kept on file by Battelle for audit purposes and for possible submission to the EPA at the conclusion of the study.

A record shall be kept by participants of all efforts and events associated with the laboratory work and of all data such as:

- Sample Handling

    Date received
    Volume and/or weight of samples
    Condition of samples
    Location and temperature of storage

- Analytical Data

  Date of extraction and GC/MS analysis
  All volumes and weights used
  Dilution and concentration factors
  Amount of internal standard added
  Internal standard area response
  Injection volume
  Relative response factors used for quantification
  Total solvent extractable content
  Major volatile compounds content
  Scan number
  Absolute and/or relative retention time
  Most intense ions
  Compound identification
  Probable molecular weight
  Total ion current chromatograms
  Library search results
  9-Track tape files
  Search system used
  Calibration results
  Mass spectrometer tuning results
  Maintenance records

Most of the above information is "required data" to be reported on forms supplied or in specified format.

Quality Control - Performance Criteria and Checks

Quality control activities start with a description of the method which must be followed without exception. Before any laboratory work is done, the method must be read and understood by all personnel who will use it. Questions regarding what is to be done must be discussed with Battelle persons before laboratory work starts. In that way uncertainties can be corrected or clarified among all cooperating laboratories and all will possess the same information. Thus, to the extent possible, the collaborators will conduct all operations in exactly the same manner.

Control will be maintained by monitoring the mass spectrometer tuning (using DFTPP or BFB), and analyzing process blanks and calibration standards. The details of the required quality control measures are described in the methods and in the QC Protocol for Fused Silica Capillary Columns.

In application of the methods it is expected that all normal care will be exercised to use properly calibrated and clean apparatus such as balances and volumetric glassware for extract preparation and to ascertain that the GC/MS system is functioning properly.

GC/MS Run Logs

Several forms are being supplied for reporting analytical information and a log of GC/MS runs. A separate log (Forms 1V and 1S) is required for each mass spectrometer used to determine volatile compounds and for each mass spectrometer used to determine semivolatile compounds. Run numbers should be consecutive from the very first calibration run to the last sample or calibration run. We envisage and suggest that the analysis runs for this program be consecutive and without interruption by other programs.

GC/MS Calibration

The daily run routine must include at least one calibration run at the beginning of the day and additional calibration runs during the day if more than 8 sample runs are made in one day.

Surrogate Standards

All samples must be spiked with surrogate compounds before extracting. The surrogate compounds are:

For Volatile Compounds

1,2-Dibromotetrafluoroethane
Bis(perfluoroisopropyl) ketone
Fluorobenzene
m-Bromobenzotrifluoride

For Semivolatile Compounds

Decafluorobiphenyl
2-Fluoroaniline
Pentafluorophenol

The spiking level used should be that which will give a concentration in the final extract used for GC/MS analyses that is equal to the level of the internal standard added assuming 100% recovery. This level is determined as described in Section 8.4 of the methods. Thus two aliquots of each sample must be screened, one for volatile compounds and one for semivolatile compounds, before aliquots can be spiked with surrogates and analyzed.

Blanks

Blanks will be defined as system or process blanks and will consist of all reagents used in sample preparation carried through the entire preparation process and finally analyzed by GC/MS. This activity will assess purity of reagents and cleanliness of apparatus and environment. It is recommended that a system blank be generated and analyzed with every batch of samples prepared or with every new batch of reagent material. A minimum of two process blanks for the volatile analyses and two process blanks for the semivolatile analyses must be run and the data reported.

CLARIFICATION OF DEVIATIONS FROM METHODS

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CLARIFICATIONS

Sample Analysis Order

The order in which samples are analyzed is not specified. However, aliquots of a given sample are to be analyzed on the same day and in sequence if possible. The order in which samples are analyzed will be recorded on the daily run log.

Recording Information on Forms

It is expected that data (and information such as sample run sequence) will be entered without delay when they are available. It is expected that there will be a daily one-over-one review of recorded data to check for errors in transcription, for completeness and for legibility. The forms are using typewriter standard space; typing data is recommended.

The protocol for reporting data is as follows:

Concentration - 3 significant figures but only one figure beyond the decimal place. For example

12300 µg/g
1230 µg/g
123 µg/g
12.3 µg/g
1.2 µg/g

In rounding data, round down when the digit to be dropped is 1, 2, 3, or 4 and up when 6, 7, 8 or 9. Round to an even number when the digit dropped is 5. For any compound not found or found but below the detection limit, enter ND. Detection limit for a compound in a given sample is defined for this purpose as

$$\frac{\text{Concentration of Internal Standard (µg/g sample)}}{\text{Response Factor x 50}}$$

Response Factor - report 3 significant figures beyond the decimal place, e.g., 1.214 or 0.789.

Relative Retention Time - report 4 figures beyond the decimal, e.g., 1.0916 or 0.8674.

Retention Time - report total seconds - NOT minutes and seconds or minutes.

Relative Abundance of Tuning Compound Ions - report two significant figures.

Spiking Surrogates

The objective of the use of surrogate compounds is to measure losses that may occur during the sample extraction and to detect immediate matrix interactions. No attempt is being made to equilibrate the surrogate compounds with sample matrix in an effort to obtain a true extraction efficiency. Therefore, the surrogates will be added along with internal standards to the extracting media rather than to the sample.

Surrogates will be added to all sample aliquots, and all calibrating solutions and blanks as described in Section 8.4 of the methods. For the purpose of this program Sections 8.2 and 8.3 of the methods are not applicable. Solutions of surrogate compounds are supplied. Therefore, the sections in the methods describing the preparation of surrogate compound solutions do not apply to this program.

Quality Control

As mentioned above, Sections 8.2 and 8.3 of the methods are not applicable to the interlaboratory study. These sections are concerned with the demonstration of an ability to generate acceptable accuracy and precision and with establishing control limits before the methods are used for routine analyses. The interlaboratory study is designed to generate that data.

Sample Storage

Waste samples and calibration solutions are to be stored in the dark and at 4°C in a refrigerator as soon as possible after receipt. Warm samples to room temperature in the dark for at least two hours but not more than 18 hours before obtaining aliquots for analysis.

Obtaining Aliquots

The waste samples shall be mixed to the extent possible before the sample container is opened and once the container is opened the triplicate aliquots for determinations of volatile compounds shall be taken without delay. After the 4 aliquots for determinations of volatile compounds have been taken, the sample shall be mixed further as appropriate before the 5 aliquots for determination of semivolatile compounds are taken. The samples vary grossly in physical characteristics and thus the requirements for mixing vary. The following mixing-aliquoting instructions are given for each sample supplied.

Sample Identification	Instructions
ILS-1	• Take aliquots for volatile compounds determinations with metal spatula. • Stir to mix the sample and take aliquots for semivolatile compound deteminations with metal spatula.
ILS-2	• Shake the sample vial to resuspend sediment and immediately take aliquots for volatile determinations with a syringe or medicine dripper. • Take the aliquots for semivolatile compound determination in the same manner while the sample is being stirred.
ILS-3	• Take aliquots for volatile compound determinations with metal spatula. • Stir to mix the sample and take aliquots for semivolatile compound determinations.
ILS-4	• Take aliquots for volatile compound determination with a metal spatula or length of glass tubing. • Stir to mix the sample and take aliquots for semivolatile compound determinations in the same manner.
ILS-5	• Take aliquots for volatile compound determinations with metal spatula or spoon. • Grind the pellets to a fine powder in a glass mortar and pestle and take aliquots for semivolatile compound determinations with a metal spatula.
ILS-6	• Take aliquots for volatile compound determinations with a metal spatula. • Stir to mix the sample and take aliquots for semivolatile compound determinations.
ILS-7	• Shake the sample vial thoroughly. Take aliquots for volatile compound determinations using a syringe or medicine dropper. • (Not to be analyzed for semivolatile compounds)
ILS-8	• Shake sample vial thoroughly. Take aliquots for volatile compound determinations using a syringe or medicine dropper. • (Not to be analyzed for semivolatile compounds).

Sample Identification	Instructions
ILS-9	• (Not to be analyzed for volatile compounds). • Take aliquots for semivolatile compound determinations using a metal spatula.

FSCC Protocol Clarifications

This section is intended to clarify various aspects of the FSCC protocol, as applied to this interlaboratory study. The semivolatile analytes, internal standards, and surrogates are listed in retention order in Table Q-1 of the FSCC protocol. For each compound listed, the indicated quantification mass must be used. For the majority of the analytes, the retention standard and quantification standard refer to the same internal standard. The exceptions are the unlabeled counterparts to the labeled column performance standards. Only for these particular compounds do the labeled column performance standards serve the additional function of quantification internal standards. Furthermore, each of seven labeled internal standards and the four labeled column performance standards is referenced to D_{10}-phenanthrene. The eleven response factors thus obtained serve as an ongoing guide to injector, column and instrument performance. Since these standards are present in every GC/MS analysis the potential exists to detect chromatographic or instrumental problems between daily calibration check runs.

Although the protocol indicates (3.3 and 8.2) the use of mass chromatograms (i.e. extracted ion current profiles) as qualitative identification criteria, the analyst may elect to utilize a commercial or custom reverse search algorithm which may not explicitly follow the criteria of using discrete mass chromatograms. The use of such an algorithm is permissible provided the reliability of the algorithm approximates that using discrete mass chromatograms.

Quality assurance is met by the analysis of a 3-level set of calibration standards described on page 8 of this section and a daily calibration check standard. Proper tuning of the mass spectrometer must be maintained throughout the study. Tuning is verified in the conventional fashion using DFTPP. Analysts experienced with environmental GC/MS analyses, particularly EPA Method 625 are generally able to approximate the proper DFTPP tuning using a conventional mass calibration compound such as perfluorotributylamine leaked directly into the source. It is recommended that the requisite mass balance and resolution be tuned in this fashion and confirmed using the DFTPP spectrum obtained from the daily calibration check standard. This procedure should eliminate the need for repeat or separate injections of DFTPP alone in order to meet the tuning criteria.

In addition to providing a DFTPP spectrum, the daily calibration check standard is designed to serve a dual purpose. The standard acts as a performance evaluation check and, if these criteria are met, functions as one of the three calibration checks standards used for the calculation of working average RRFs as described in 10.3 of the protocol. The average RRFs thus obtained are to be applied only to those sample analyses performed during the same day (or 8-hour analysis session) as the daily calibration check standard. This usage requires that the calibration check standard be analyzed at the beginning of each day that samples are analyzed.

The three level calibration check (20, 50, 200) described in 8.3.5 and 9.3 should be performed at the beginning of the analytical efforts associated with this study and at subsequent intervals not to internal standards, compute the area ratio, $\frac{A\ unlab}{A\ lab}$, at each of the three levels and calculate the correlation coefficient with respect to the amount of unlabeled analyte. For a given unlabeled-labeled pair, the correlation coefficient (r) can be calculated as follows:

$$r = \frac{3\Sigma xiyi - 270\Sigma yi}{236.22\ [3\Sigma yi^2 - (\Sigma yi)^2]^{1/2}}$$

Where:

yi = area ratio at amount xi
xi = 20, 50, or 200.

A correlation coefficient of 0.9990 or higher for each of the 8 compounds verifies that the dynamic range and linearity of the method are not being compromised by offsets, saturation or non-linear instrument gain. The eight labeled standards provided are of sufficient isotopic purity and substitution that isotopic dilution corrections to the area ratios are not required.

Retention and Response of Volatiles

Several of the listed volatile compounds have demonstrated, in a single laboratory evaluation, weak or inconsistent recoveries using the purge and trap method. Those compounds consistently recovered and also the internal standards and surrogates are shown in retention order in Table 5. The quantification mass shown for each compound must be used by the participating laboratories. These masses have been chosen based on a number of factors which include proximity to the mass of the internal standard, relative intensity and chromatographic resolution within the calibration mixture. As with the semivolatile standards, three of the internal standards are referenced to the fourth standard (D_6-benzene) in order to provide a performance check for each analysis. The response factors listed are to serve as a guide only. An updated list will be provided based on further investigations of these compounds.

Identification of Unlisted Volatile and Semivolatile Compounds

For each sample analyzed, the participant is to assign a tentative identification and semiquantitative estimate for significant GC peaks not corresponding to one of the listed compounds associated with the method used. Significance shall be defined as a GC peak whose height is at least 10 percent of the GC peak corresponding to D_6-benzene (volatile) or D_{10}-phenanthrene (semivolatiles). The semiquantitative estimate is to be calculated using D_6-benzene phenanthrene as the internal standard based on the total ion current areas of the unknown and the internal standard with an assumed response factor of 1.0. A maximum of 10 unlisted compounds are to be reported for each semivolatile analysis and 10 unlisted compounds are to be reported for each volatile analysis. If more than 10 peaks meet the significance criteria, the 10 largest peaks should be chosen. Forms S and 3V are to be used to summarize data obtained for these compounds. The data for each compound to be listed on these forms includes the estimated amount, retention time in seconds (for volatiles) or relative retention time (relative to D_{10}-phenanthrene for semivolatiles) and the integer masses and relative intensities of the four most abundant ions in the background corrected mass spectrum. In addition, the participant is to provide a copy of the total ion chromatogram from each GC/MS run with scan numbers indicated, a bar graph spectrum of each unlisted compound with the scan number indicated and a copy of the printout with the scan number indicated obtained from a forward library search using the resident library search algorithm in the participant's data system. The search should be conducted using the most recently available edition of the EPA/NIH mass spectral data base.

Performance Evaluation Samples

The concentrations of compounds in the two prepared extracts have been adjusted to permit analysis with no further treatment other than the addition of the specified amount of internal standard. One milliliter of the extract to be analyzed for semivolatile compounds is to be mixed with 330 µL of Semivolatile Internal Standard solution F (200 µg/mL) and 1 µL of the mixture is to be injected into the GC/MS. An 80-µL sample of the extract to be analyzed for volatile compounds is to be injected into the purging chamber containing 12.5 µL of internal standard (20 µg/mL). The internal standard is prepared by diluting 100 µL of Volatile Internal Standard Solution I (200 µg/mL) to 1.0 mL with reagent tetraglyme.

The methods for the determination of semivolatile and volatile organic compounds included in this instruction manual are to be followed for the extraction and analysis of the waste sample, ILS-1, which is being used as a performance evaluation sample.

Calibration Solutions

The calibration solutions of volatile compounds provided are Supelco's Purgeable A (4-8815), Supelco's Purgeable B (4-8816), Supelco's Purgeable C (4-8817), and Volatile Calibration solutions G, J and K. The concentration of each component in these six calibration solutions is 200 µg/mL. The volatile surrogate standard solution provided contains 10,000 µg/mL of each surrogate. A calibration mixture containing 10 µg/mL of each of the volatile compounds is prepared by taking 50 µL of each of the six calibration solutions and 50 µL of a 1:50 dilution (in reagent tetraglyme) of the surrogate standard solution and diluting to 1.0 mL with reagent tetraglyme. Four calibration levels, 25, 100, 250, and 1000 ng, are to be analyzed once at the beginning of each week. These are obtained by using 2.5, 10, 25 and 100 µL, respectively, of the calibration mixture. The results obtained from the analysis of the low level standard, 25 ng, are to be reported but not used in any average response factor calculations. A single calibration level, 250 ng, is to be used for all subsequent calibrations. This calibration level must be anayzed at the beginning of each day that samples are analyzed.

The calibration solutions of semivolatile compounds provided are Semivolatile Calibration Solutions A, B, C, and D. The concentrations of each component in these four solutions are 100, 1000, 500, and 1000 µg/mL, respectively. The Semivolatile Surrogate Standard Solution E provided contains 10,000 µg/mL of each surrogate. A calibration mixture containing 267 µg/mL of each of the semivolatile compounds in Solutions B, C, and E and 133 µg/mL of each of the semivolatile compounds in Solution D is prepared by mixing 200 µL of B, 400 µL of C, 100 µL of D, 20 µL of E and 30 µL of methylene chloride. The resulting mixture, when mixed with 250 µL of the 200 µl/mL Semivolatile Internal Standard Solution F, will provide a calibration standard containing 200 µg/mL of each compound in Solutions B, C, and E, 100 µg/mL of each compound in Solution D and 50 µg/mL of each internal standard and performance standard.

A calibration mixture containing 66.7 µg/mL of each of the semivolatile compounds in Solutions A to E is prepared by mixing 1.00 mL of A, 100 µL of B, 200 µL of C, 100 µL of D, 10 µL of E, and 90 µL of methylene chloride. Calibration mixtures containing 26.7 µg/mL and 6.67 µg/mL are prepared by diluting the 66.7 µg/mL mixture by factors of 2.5 and 10, respectively. The resulting mixtures, when 750 µL is mixed with 250 µL of the 200 µg/mL internal standard solution will provide calibration standards at 5, 20 and 50 µg/mL, respectively, containing all of the internal standards and performance standards at 50 µg/mL. Each of the four calibration concentrations levels is to be analyzed once at the beginning of each week. The results obtained from the analysis of the low level standard, 5 µg/mL, are to be reported but not used in any average response factor calculations.

Prescreening Studies

Prior to the extraction and analysis of three replicate aliquots for the determination of volatile compounds and/or three replicate aliquots for the determination of semivolatile compounds from each waste sample, aliquots must be taken for prescreening studies to determine the approximate level of major volatile compounds and/or major semivolatile compounds present. The amount of the surrogate compounds to be added to each replicate will be determined by these prescreening studies. The prescreening procedures are described in the methods for the determination of volatile and semivolatile compounds. For volatile components, an aliquot is extracted with n-hexadecane and the extract is analyzed by packed column gas-chromatography. For semivolatile components, an aliquot is extracted with methylene chloride and the extract is analyzed by fused silica or glass capillary column gas chromatography (DB-5 SE-54 or equivalent).

The prescreening for the determination of volatile compounds will give the estimated major volatile compounds content (MVCC). The prescreening for volatile content is to be conducted only once and the MVCC is to be reported at the top of Form 2V. The prescreening for the determination of semivolatile compounds will give the total solvent extractable content (TSEC), determined gravimetrically, as well as an indication of the amount of dilution or concentration of the extract required prior to GC/MS analysis. The prescreening for semivolatile content is part of the general extraction scheme. The TSEC value from the initial prescreening does not need to be reported. However, the TSEC is to be determined on the extract from each of the three replicates extracted for GC/MS analysis and the TSEC values are to be reported at the top of Form 2S.

The total amount of sample required for the determination of volatile compounds is 7 grams. This amount includes one gram for a prescreening run and three 2-gram aliquots for extraction and GC/MS analysis. The total amount of sample required for the determination of semivolatile compounds is 15 grams. This amount includes three grams for an acid/base screen, 3 grams for a prescreening run and three 3-gram aliquots for extraction and GC/MS analysis.

In order to minimize the loss of volatile compounds, we recommend that the aliquots for volatile analyses be taken before the aliquots for semivolatile analyses are taken.

Foaming During Purge and Trap

The use of tetraglyme increases the degree of foaming that occurs. It is necessary to use purging chambers that have a bulb at the top or are otherwise designed to revent foam or liquid from being carried into the transfer line.

Gel Permeation Chromatography

A cleanup step involving gel permeation chromatography (GPC) is described in Section 11 of the method for the determination of semivolatile compounds. This cleanup step is useful for the analysis of samples in which most of the solvent extractable material is polymeric or high molecular weight. GPC should not be used as a cleanup step for any of the samples in the interlaboratory study. No GPC capability is required.

GC/MS Search Information

The qualitative criteria specify that a listed compound found in an unknown must meet the following minimum specifications:

(1) The retention time must be within ± 8 seconds of that calculated from the relative retention time (RRT).

RRTs should be updated from the daily calibration run...

(2) All ions above 10% relative abundance in a standard must be present and within ± 20 percent of the relative abundance in the standard.

(3) All characteristic ions defined in (2) above must each exhibit a GC maximum within ± one scan (i.e., three consecutive scans).

It is recognized that a search for this large number of compounds in a particular set of sample data could require an extensive amount of effort on the part of the participant, particularly if one attempts to interactively define and plot mass chromatograms. Most major GC/MS data systems contain packaged or modular reverse search programs which are designed to ease this burden on the user. The degree of automation of these programs varies, however, many programs are designed to search sequentially for a set of compounds in a completely unattended fashion. Although a particular program may not explicitly implement the above identification criteria in the search algorithm, the program may be used for this study provided that the performance of the program approximates user interactive approach using GC/MS chromatograms. It is the participant's responsibility to ensure that a reverse search program, if used, functions in a reliable fashion.

In addition to the reverse search for listed compounds, a forward library search is to be performed on background corrected spectra obtained from GC peaks not associated with one of the listed compounds. Most commercial data systems provide this capability as well as an on-line mass spectral library derived from the EPA/NIH data base. Since a variety of forward and reverse research programs are available among the participating laboratories no further direction is given for conducting the search programs.

SUMMARY OF DELIVERABLES

Each participating laboratory is required to meet all due dates listed in the Schedule. The following data are to be submitted by each participating laboratory.

1. A run log of the GC/MS analyses performed for the study including run number, identity of run, date of extraction, date of analysis, and the area counts and retention time of the primary internal standard (Forms 1V and 1S).
2. Amount, retention time or relative retention time, and response factors used for each of the 200 listed compounds detected in each sample analyzed, including process blanks (Forms 2V and 2S).
3. Amount, tentative identification, most intense ions, and retention time or relative retention time for each of the 10 major unlisted volatile compounds and 10 major unlisted semivolatile compounds found in each sample (Forms 3V and 3S).
4. Relative ion abundances of the mass spectrometer tuning compound for each tuning check run. (Forms 4V and 4S).
5. Retention time and response factor for each internal standard in each GC/MS run (Forms 5/6V, 5S, and 6S).
6. Recovery, concentration added, internal standard level, retention time (Volatiles) or relative retention time (Semivolatiles) and response factor used for each surrogate standard in each sample (Forms 7V and 7S).
7. Response factor and retention time (Volatiles) or relative retention time (Semivolatiles) found for each of the listed compounds in each calibration run (Forms 8V, 8S, 9V, and 9S).
8. Total solvent extractable content and major volatile compounds content determined during the prescreening of each sample (Forms 2V and 2S).
9. A copy of the total ion chromatogram from each GC/MS run.
10. The background corrected mass spectrum and library search results, both identified by scan number, for each unlisted compound reported.
11. A brief narrative description of the GC/MS system used to acquire data and the computer software and/or manual processes used to obtain the qualitative and quantitative results reported.
12. Comments and recommendations regarding the use of the methods (Program Review Inquiry Form).

PROGRAM REVIEW INQUIRY

FOR

COLLABORATORS IN THE INTERLABORATORY STUDY OF METHODOLOGY FOR ORGANIC CONSTITUENTS OF HAZARDOUS WASTE

1981

The purpose of this inquiry is to elicit pertinent information and recommendations from operators involved in this study regarding any problems encountered in carrying out their part of the study.

Your response will be an important aid in providing clear and unambiguous descriptions of the techniques and procedures of the method.

Therefore, respond to all questions and requests. If a particular request is outside your experience, enter "no opinion".

A separate inquiry form is to be filled out by every person connected with the study. Use additional sheets for any additional space necessary for lengthy comments.

Name of Company ____________________

Name ____________________

Function or Title ____________________

How involved with this study (Administration, sample preparation, analysis, QC, etc.)? ____________________

____

____

Format and Style of Instructions

Were instructions organized logically and written concisely? ____________________

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What improvements can you suggest? (You may want to return an edited copy of the instructions with your suggestions.) ______________________________

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Sample Packaging and Preservation

Describe any problems encountered? ______________________________

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Describe your treatment of the problems? ______________________________

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Describe changes that you recommend? ______________________________

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Obtaining Aliquots

Were instructions clear and understandable? If not, please explain.

Describe any problems encountered and your treatment of the problems.

Describe changes that you recommend.

Sample Extraction

Were instructions clear and understandable? If not, please explain.

Describe any problems encountered and your treatment of the problems.

Describe changes that you recommend.

GC/MS Procedures

Were instructions clear and understandable? If not, please explain.

Describe any problems encountered and your treatment of the problems.

Describe changes that you recommend.

QC Requirements

Were instructions clear and understandable? If not, please explain.

Was protocol for daily analyses and for GC/MS performance adequate for control of analyses?

Describe any problems encountered with QC requirements.

Describe changes that you recommend.

Data Sheets

Were instructions clear and understandable? If not, please explain.

What changes do you recommend?

Other Comments

Enter here any comments or recommendations for items not covered above.

ADDENDUM 1

Response Factors of Semivolatile Compounds

Since 1-chloronaphthalene frequently coelutes and interferes with the quantification of D_{10}-biphenyl, we have deleted D_{10}-biphenyl as an internal standard and have replaced it with D_{10}-acenaphthene. We have revised Table Q-1 that appeared in the Quality Assurance section of the manual to change the relative retention times and response factors for those compounds that were previously referenced to D_{10}-biphenyl. Your search libraries will need to be revised to reflect these changes. We have also changed many of the other response factors and some of the other relative retention times to reflect more recent and more reliable data. Replace Table Q-1 dated December 17, 1981 with the enclosed Table Q-1 dated July 23, 1982.

Performance Criteria for Detemination of Semivolatile Compounds

Prior to the analysis of samples each laboratory must demonstrate that the tuning and sensitivity of the GC/MS system are acceptable and that response factors obtained for calibration standards at the 50 ng/μL level are acceptable. In order to minimize the amount of effort required to check response factors a check list of 20 representative compounds has been selected. These compounds, the response factors specified for the compounds (using the reference internal standards designated in Table Q-1), and the acceptable ranges for the response factors are given in Table 2. The acceptable ranges for the response factors are given in Table 2. The acceptable ranges represent an allowable variation of ±40% from the specified response factors. If acceptable response factors are obtained for these 20 compounds, it is reasonable to expect that all compounds listed in Table Q-1, including surrogates and deuterated standards, with the exception of the 11 compounds noted with a double star after their response factor, will be detectable and will have response factors of at least 50% of the listed values. If any of the unstarred compounds in Table Q-1 is not detected in a calibration run at the 50 ng/μL level or if a response factor is less than 50% of the listed value, the search and quantification should be checked manually to see if there is a problem with the computer routine used.

The required daily GC/MS run protocol for the determination of semivolatile compounds is as follows:

- Tune mass spectrometer with DFTPP introduced via the GC column
- Make first calibration run using a 50 ng/μL standard
- Make sample analysis runs
- Make second calibration run using a 50 ng/μL standard

The DFTPP relative ion abundances must meet all EPA (Eichelberger) criteria (given in Table 1 of the method).

The sensitivity setting of the mass spectrometer must be such that the area obtained for D_{10}-phenanthrene in the first calibration run of the day is at least 50 times the area that represents a reliable quantification limit and less than one-fourth of the minimum area that represents significant saturation.

The response factors obtained from the first calibration run of each day for all of the 20 compounds shown in Table 2 must agree within ±40% of the RF's specified (i.e. within the acceptable range given).

The response factors obtained from the first calibration run of the day may be used for the quantification of the listed compounds found in the samples analyzed during the day if the response factors obtained from the second calibration run for all of the 20 compounds shown in Table 2 agree within ±20% of those obtained from the first calibration run of the day. (In accordance with Section 7.4 of the method).

If the response factors obtained from the second calibration run for one or more of the 20 compounds shown in Table 2 varies by more than 20 percent but less than 40 percent from those obtained from the first calibration run of the day, the average RFs obtained from the first and second calibration runs must be used for the quantification of all listed compounds found in the samples analyzed during the day.

If the response factors obtained from the second calibration run for one or more of the 20 compounds shown in Table 2 varies by more than 40 percent from those obtained from the first calibration run of the day (making it impossible to meet the requirement of Section 7.4 of the method), all of the sample analyses for the day must be rejected.

The 20 percent and 40 percent variations mentioned above refer to relative amounts. For example, the acceptable range for the response factor of 2,6-dichlorophenol is 0.30 ± 40% or 0.18 to 0.42.

The above performance protocol is shown schematically in Figure 1. The DFTPP tuning check can be done either as a separate GC run or in combination with the calibration run.

Deliverables

DFTPP relative ion abundance data is to be reported only for tuning checks made at least once each day (rather than from every run as previously requested).

Items 6 and 7 of the Summary of Deliverables section of the manual specify that "retention time or relative retention time" is to be reported. Retention time applied only to determinations of volatile organic compounds and relative retention time applies only to determinations of semivolatile organic compounds. A revised "Summary of Deliverables" section dated July 23, 1982 is enclosed to replace the one dated December 17, 1981.

In calculating averages and relative standard deviations, do not include zeros nor "not found" data.

Because of differences in the quality (repeatability) of different data parameters there are differences in the number of digits to be reported. The protocol for reporting is given on pages 1 and 2 of the Clarifications section of the Manual.

Be sure to fill out each report form completely; especially remember to include the laboratory name and sample number (not run number).

Be sure to include in your final data package to us responses to points 11 and 12 on the "Summary of Deliverables" (narrative description of GC/MS Systems and comments on the program review inquiry form).

Check dilution factors, internal standard levels, and calculations carefully to insure that the correct values are reported for the amounts found as μg/g.

Miscellaneous Notes

Poor chromatography is frequently obtained for pyridines. For this reason double stars have been placed after their response factors in Table Q-1. Simply report whatever results you get for pyridines without trying to improve their chromatography.

Tetraglyme that is satisfactorily pure is being sought and availability will be announced by July 30.

We anticipate that participants have sufficient supplies of standard solutions to complete this study. However, there is a small inventory of some of these solutions that will be distributed if necessary. Each participant is expected to take care of his own needs for compounds in Supelco Purgeable A, B, and C.

Sample ILS-5, for determination of semivolatile organic compounds, is the only sample in this study that requires pulverization. Use a mortar and pestle made of glass or agate instead of porcelain to avoid losses caused by absorption.

As many of you may have guessed from looking at your results for the performance evaluation samples, ILS-10 was an extract of ILS-1. Thus by comparing your results for the two samples you can get an indication of how your extraction efficiency and dilution scheme compared with ours. In most cases in which fewer compounds were reported for ILS-1 than for ILS-10, the extract was diluted considerably more than we diluted. In order to obtain satisfactory results for the remaining samples, careful attention will need to be given to the GC/FID screening. We recommend that you screen each extract at the final concentration intended for GC/MS analysis (taking into account the dilution resulting from the addition of the internal standard solution) and make sure that the average peak height of the five largest peaks or the height of a broad unresolved envelop of peaks is at least as great as that of phenanthrene at a concentration of 100 μg/mL recommended in Section 10.6 of the method). If the total ion current chromatogram indicated considerably lower levels of compounds than indicated by the FID chromatogram, the extract may need to be concentrated further and reanalyzed.

Many of the detection and quantification problems experienced by several of the laboratories seemed to be attributable to an inability of the computer search routines used to handle such complex and dirty samples. The samples are representative of "real world" samples; but, the extracts are frequently dirtier and more complex than extracts of water samples. You may find that manual searching will significantly decrease the number of false negatives and improve the reliability of the quantifications in many cases.

Several corrections have been made in the report forms. These include the addition of the surrogates to Forms 8V, 9V, 8S, and 9S and the correction of names or spellings for Cpd. 15 on Form 2V, Cpds. 91, 92, 104, and 138 on form 2S, and Cpds. 66 and 101 on Form 8S. A complete set of the corrected forms, dated July 23, 1982, is enclosed. Additional sets of Forms 2V and 2S are also enclosed. Please use these latest forms for reporting your data. Do not use forms for reporting your data. Do not use forms dated December 17, 1981.

We are deeply aware of the amount of effort and attention to detail this study requires and we appreciate the patience and sense of cooperation exhibited thus far. We're confident that the results of the study will make the effort worthwhile.

ADDENDUM 2

Clarification of Section 11.3.2 of Volatiles Method

Several laboratories have indicated some difficulty in understanding the calculations suggested in Section 11.3.2 of the method for the determination of volatile organic compounds. The confusion has been caused by some errors in the writeup that resulted when MVCC was changed from mg/g to µg/g during the method development. One laboratory has also indicated that some guidelines for determining the amount of surrogate standard solution to be used would be helpful. We have therefore revised Section 11.3.2 to clarify these matters. The revised section is enclosed. The specific revisions are enclosed in brackets.

Screening Protocol for Determining MVCC

One of the samples to be analyzed for volatile compounds has very substantial amounts of compounds in the n-hexadecane extract that elute very close to n-dodecane. The MVCC value for that sample will vary widely depending upon whether or not the material that elutes near n-dodecane is included. Since material that elutes near n-dodecane would have a boiling point of over 200°C and would not contribute significantly to the purgeable material, we are changing the screening procedure in Section 11.1 to use n-decane instead of n-dodecane as the cutoff pont. It is also acceptable to use n-decane instead of n-nonane for determining an area response factor. Please make these changes in Section 11.1 of your copy of the method. Since the changes should be quite clear, we are not sending a revised Section 11.1.

Surrogate Spiking of Tetraglyme-Soluble Samples

Section 11.2 of the method for determining volatile compounds provides for the addition of the surrogate standard prior to the extraction of the 2-gram sample. However, if the sample is completely soluble in tetraglyme and no extraction is involved, as is the case for ILS-8, the chlorinated ethanes waste, it is acceptable to add an apppropriate amount of the surrogate standard to an aliquot of the tetraglyme solution of the sample in order to conserve surrogate standard.

Quantification of Unlisted Compounds

The semiquantitative estimation of the levels of unlisted compounds is addressed on page 7 of the Clarifications section of the instruction manual. The instructions state that quantification should be based on the total ion current areas of the unknown and the internal standard.

However, in some cases there may be large amounts of interfering compounds that coelute with the internal standard and cause large errors in the total ion current areas. Therefore, whenever there are coeluting compounds present that affect the total ion current area of the internal standard, e.g., the presence of benzene that interferes with D_6-benzene, use the characteristic ion of the internal standard for the quantification and correct the amount found by multiplying by the ratio of the characteristic ion area to total ion area for the internal standard. The ratio of the characteristic ion area to total ion area for the internal standard can be obtained from the data from a process blank run.

APPENDIX F

VOLATILES REPORT FORMS

GC/MS RUN LOG FOR VOLATILE COMPOUND ANALYSES

Laboratory ID ________

Run No.	Date	Run Identification	Area of D_6-Benzene	RT of D_6-Benzene, seconds	Date of Sample Extn.
Avg.					
% RSD					

Form IV

LISTED VOLATILE COMPOUNDS FOUND

Laboratory ID ________

Sample ID ________

Concentration of Internal Standard, μg/g

Rep 1________ Rep 2________ Rep 3________

Major Volatile Compounds Content, μg/g ________

Compound	Amount Found, μg/g			RT Found, seconds			RF Used for Quantitation		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
1. Chloromethane									
2. Bromomethane									
3. Vinyl chloride									
4. Chloroethane									
5. Methylene chloride									
6. Acetone									
7. Dimethyl sulfide									
8. Acrolein									
9. Bromoethane									
10. Acrylonitrile									
11. Carbon disulfide									
12. Propionitrile									
13. 2-Chloropropane									
14. Allyl chloride									
15. 1, 1-Dichloroethylene									
16. trans-1, 2-Dichloroethylene									
17. 1, 1-Dichloroethane									
18. Diethyl ether									
19. Chloroform									
20. 1, 1, 2-Trichlorotrifluoroethane									
21. 2-Butanone									
22. 1, 2-Dichloroethane									
23. Dibromomethane									
24. 2-Chloroacrylonitrile									
25. 1, 1, 1-Trichloroethane									
26. Carbon tetrachloride									
27. Epichlorohydrin									
28. Bromodichloromethane									
29. Methyl acrylate									
30. Dichloroacetonitrile									
31. Vinyl acetate									
32. 1-Chlorobutane									
33. 1, 2-Dichloropropane									
34. Dimethyl disulfide									
35. trans-1, 3-Dichloropropene									

Form 2V

LISTED VOLATILE COMPOUNDS FOUND

Laboratory ID ____________

Sample ID ____________

Concentration of Internal Standard, μg/g

Rep 1 __________ Rep 2 __________ Rep 3 __________

Major Volatile Compounds Content, μg/g ________

Compound	Amount Found, μg/g			RT Found, seconds			RF Used for Quantification		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
36. Trichloroethylene									
37. Dibromochloromethane									
38. 1, 1, 2-Trichloroethane									
39. cis-1, 3-Dichloropropene									
40. Benzene									
41. Dibromoethane									
42. 2-Chloroethylvinyl ether									
43. Methyl methacrylate									
44. Bromoform									
45. 4-Methyl-2-pentanone									
46. 2-Hexanone									
47. 1, 1, 2, 2-Tetrachloroethane									
48. Tetrachloroethylene									
49. Toluene									
50. Chlorobenzene									
51. Ethylbenzene									
52. Styrene									
53. o-Xylene									

Form 2

UNLISTED VOLATILE COMPOUNDS FOUND

Laboratory ID __________

Sample ID __________

Tentative Identification	Amount Found, µg/g			Retention Time, seconds			Characteristic Ions (Relative Intensity)			
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Ion (RI)	Ion (RI)	Ion (RI)	Ion (RI)

Form 3V

RELATIVE ABUNDANCES BFB IONS IN VOLATILE COMPOUND ANALYSES

Laboratory ID ________

Run No.	Relative Abundance of Given Ion								
	50	75	95	96	173	174	175	176	177
Avg.									
% RSD									

Form 4V

RETENTION TIMES AND RESPONSE FACTORS OF VOLATILE INTERNAL STANDARDS

Laboratory ID ____________

Run No.	Retention Time of Given Internal Standard, seconds				Response Factor of Given Internal Standard		
	DCE	Ben	EtB	BFB	DCE	EtB	BFB
Avg.							
% RSD							

CE = D_4-1,2-Dichloroethane; Ben = D_6-Benzene; EtB = D_{10}-Ethylbenzene; BFB = 4-Bromofluorobenzene.

Form 5/SV

VOLATILE SURROGATE STANDARD DATA

Laboratory ID ___________

Run No.	Int. Std. Level, µg/l	Conc. of Surrogates Added, µg/l	RT of Given Surrogate, seconds				RF Used for Given Surrogate				Percent Recovery of Given Surrogate			
			DTE	BPK	FB	BBT	DTE	BPK	FB	BBT	DTE	BPK	FB	BBT
Avg.														
% RSD														

Compound Code:
DTE = 1,2-Dibromotetrafluoroethane
BPK = Bis(perfluoroisopropyl) ketone
FB = Fluorobenzene
BBT = m-Bromobenzotrifluoride

Form 7V

RETENTION TIMES OF VOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID ___________

Compound	Retention Time, seconds, Obtained From GC-MS Calibration Run of Given Run Number																	Avg.	% RSD
1. ClMethane																			
2. BrMethane																			
3. Vinyl Chlor																			
4. ClEthane																			
5. Methylene Cl																			
6. Acetone																			
7. DMe Sulfide																			
8. Acrolein																			
9. BrEthane																			
10. AcryloCN																			
11. Carbon Disulf																			
12. PropioCN																			
13. 2-ClPropane																			
14. Allyl Chloride																			
15. 1, 1-DClEthene																			
16. t-1, 2-DClEthen																			
17. 1, 1-DClEthane																			
18. Diethyl Etner																			
19. Chloroform																			
20. TCTFEthane																			
21. 2-Butanone																			
22. 1, 2-DCEthane																			
23. DBrMethane																			
24. 2-ClAcryloCN																			
25. 1, 1, 1-TClEthe																			
26. Carbon TetCl																			
27. EpiChlorHyd																			
28. BrDClMethane																			
29. Me Acrylate																			
30. DClAcetoCN																			
31. Vinyl acetate																			
32. 1-ClButane																			
33. 1, 2-DClPropan																			
34. DMe Disulfide																			
35. t-1, 3-DClPrope																			
36. TriClEthene																			
37. DBrClMethane																			

Form 8V

RETENTION TIMES OF VOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID ____________

Compound	Retention Times, seconds, Obtained From GC-MS Calibration Run of Given Run Number																	Avg.	% RSD
38. 1, 1, 2-TClEtha																			
39. c-1, 3-DClPrope																			
40. Benzene																			
41. DBrEthane																			
42. 2-ClEtV Ether																			
43. Me Methacryl																			
44. Bromoform																			
45. 4-Me-2-Penone																			
46. 2-Hexanone																			
47. TetraClEthane																			
48. TetraClEthene																			
49. Toluene																			
50. ClBenzene																			
51. EtBenzene																			
52. Styrene																			
53. o-Xylene																			
S1. 1,2-DBrTetFET																			
S2. BisPerFlPrKeT																			
S3. F Benzene																			
S4. m-BrBenzoTriF																			

Form 8V

RESPONSE FACTORS FROM VOLATILE CALIBRATIONS RUNS

Laboratory ID __________

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																Avg.	% RSD
1. ClMethane																		
2. BrMethane																		
3. Vinyl Chlor																		
4. ClEthane																		
5. Methylene Cl																		
6. Acetone																		
7. DiMe Sulfide																		
8. Acrolein																		
9. BrEthene																		
10. AcryloCN																		
11. Carbon Disulf																		
12. PropioCN																		
13. 2-ClPropen																		
14. Allyl Chloride																		
15. 1, 1-DClEthene																		
16. t-1, 2-DClEthen																		
17. 1, 1-DClEthane																		
18. Diethyl Ether																		
19. Chloroform																		
20. TCTFEthane																		
21. 2-Butanone																		
22. 1, 2-DCEthane																		
23. DBrMethane																		
24. 2-ClAcryloCN																		
25. 1, 1, 1-TClEtha																		
26. Carbon TeTcl																		
27. EpiChlorHyd																		
28. BrDClMethane																		
29. Me Acrylate																		
30. DClAcetoCN																		
31. Vinyl acetate																		
32. 1-ClButane																		
33. 1, 2-DClPropan																		
34. DiMe Disulf																		
35. t-1, 3-DClPrope																		
36. TriClEthene																		
37. DBrClMethane																		

Form 9V

Laboratory ID ____________

RESPONSE FACTORS FROM VOLATILE CALIBRATION RUNS

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																	
																		Avg.	% RSD
38. 1, 1, 2-TClEthe																			
39. c-1, 3-DClPrope																			
40. Benzene																			
41. DBrEthane																			
42. 2-ClEtV Ether																			
43. Me Methacryl																			
44. Bromoform																			
45. 4-Me-2-Pentano																			
46. 2-Hexanone																			
47. TetraClEthene																			
48. TetraClEthane																			
49. Toluene																			
50. ClBenzene																			
51. EtBenzene																			
52. Styrene																			
53. o-Xylene																			
S1. 1,2-DBrTetFEt																			
S2. BisPerFlPrKet																			
S3. F Benzene																			
S4. m-BrBenzoTriF																			

Form 9V

APPENDIX G

SEMIVOLATILES REPORT FORMS

GC/MS RUN LOG FOR SEMIVOLATILE COMPOUND ANALYSES

Laboratory ID __________

Run No.	Date	Run Identification	Area of D_{10}-Phen.	RT of D_{10}-Phen., seconds	Date of Sample Extn.
Avg.					
% RSD					

Form 16

LISTED SEMIVOLATILE COMPOUND FOUND

Laboratory ID __________

Sample ID __________

Concentration of Internal Standard, μg/g

Rep 1__________ Rep 2__________ Rep 3 __________

Total Solvent Extractable Content, mg/g

Rep 1__________ Rep 2__________ Rep 3__________

Compound	Amount Found, μg/g			RRT Found			RF Used for Quantification		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
1. 4-Methylpyridine									
2. 1, 4-Dichlorobutane									
3. Anisole									
4. Bromobenzene									
5. 2, 4-Dimethylpyridine									
6. 4-Chlorotoluene									
7. Benzaldehyde									
8. Thiophenol									
9. Pentachloroethane									
10. Aniline									
11. Phenol									
12. Bis (2-chloroethyl) ether									
13. 2-Chlorophenol									
14. 1, 2, 4-Trimethylbenzene									
15. 2, 4, 6-Trimethylpyridine									
16. 1, 4-Dichlorobenzene									
17. Benzyl chloride									
18. Benzyl alcohol									
19. 1, 2-Dichlorobenzene									
20. 2-Methylphenol									
21. N-Methylaniline									
22. Acetophenone									
23. 4-Methylphenol									
24. 4-Methylaniline									
25. Hexachloroethane									
26. Nitrobenzene									
27. N, N-Dimethylaniline									
28. 4-t Butylpyridine									
29. 1, 2, 4, 5-Tetramethylbenzene									
30. 4-Chlorobenzaldehyde									
31. 2-Nitrophenol									
32. Benzal chloride									
33. 2, 4-Dimethylphenol									
34. 2-Nitrotoluene									
35. Tetralin									

Form 28

LISTED SEMIVOLATILE COMPOUNDS FOUND

Laboratory ID ________

Sample ID ________

Concentration of Internal Standard, µg/g

Rep 1________ Rep 2________ Rep 3 ________

Total Solvent Extractable Content, mg/g

Rep 1________ Rep 2________ Rep 3________

Compound	Amount Found, µg/g			RRT Found			RF Used for Quantification		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
36. Propiophenone									
37. 2, 6-Dimethylaniline									
38. Benzoic acid									
39. 2, 6-Dichlorophenol									
40. 1, 2, 4-Trichlorobenzene									
41. Naphthalene									
42. 4-Chlorophenol									
43. 4-Chloroaniline									
44. 2, 4-Dichlorophenol									
45. Hexachloropropene									
46. 4-Nitrotoluene									
47. Hexachlorobutadiene									
48. Benzotrichloride									
49. 1-Chloro-4-nitrobenzene									
50. Quinoline									
51. Bis (2-chloroethoxy) ethane									
52. 4-Chloro-3-methylphenol									
53. 4-t-Butylphenol									
54. 2-Methylnaphthalene									
55. 4-Bromoaniline									
56. 4-Chloro-2-methylaniline									
57. 4-Chlorobenzoic acid									
58. 1, 2, 4, 5-Tetrachlorobenzene									
59. 2, 4, 6-Trichlorophenol									
60. 2, 4, 5-Trichlorophenol									
61. Acetanilide									
62. 2-Chloronaphthalene									
63. Biphenyl									
64. 1-Chloronaphthalene									
65. 4-Methylquinoline									
66. 2-Ethylnaphthalene									
67. Phenyl ether									
68. 2-Nitroaniline									
69. 4-Bromobenzoic acid									
70. 3, 4-Dichloroaniline									

Form 23

LISTED SEMIVOLATILE COMPOUNDS FOUND

Laboratory ID ____________

Sample ID ____________

Concentration of Internal Standard, µg/g

Rep 1__________ Rep 2__________ Rep 3 __________

Total Solvent Extractable Content, mg/g

Rep 1 __________ Rep 2__________ Rep 3__________

Compound	Amount Found, µg/g			RRT Found			RF Used for Quantification		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
71. 2-Chloro-4-nitrophenol									
72. Acenaphthylene									
73. 2, 3-Dimethylnaphthalene									
74. 1, 3-Dinitrobenzene									
75. Dimethyl phthalate									
76. 2, 6-Dinitrotoluene									
77. 3-Nitroaniline									
78. Acenaphthene									
79. 2, 4-Di-t-butylphenol									
80. 2, 4-Dinitrophenol									
81. 2-Naphthol									
82. 2, 6-Di-t-butyl-4-methylphenol									
83. Dibenzofuran									
84. 4-Nitrophenol									
85. Pentachlorobenzene									
86. 2, 4-Dinitrotoluene									
87. 1-Aminonaphthalene									
88. 2, 4, 5-Trichloroaniline									
89. 2, 4-Dinitrochlorobenzene									
90. Fluorene									
91. 4-Chlorophenyl phenyl ether									
92. 4-Chloro-2-nitroaniline									
93. 4-Nitroaniline									
94. 2-Methyl-4, 6-dinitrophenol									
95. Diphenylamine									
96. Azobenzene									
97. Trifluralin									
98. 2-Chloro-4-nitroaniline									
99. 4-Hydroxybiphenyl									
100. Hexachlorobenzene									
101. 2, 6-Dichloro-4-nitroaniline									
102. 2, 4-Dichlorophenoxyacetic acid									
103. 4-Aminobiphenyl									
104. Pentachloro phenol									
105. 3, 3'-Dichlorobiphenyl									

Form 25

LISTED SEMIVOLATILE COMPOUNDS FOUND

Laboratory ID ____________

Sample ID ____________

	Concentration of Internal Standard, µg/g Rep 1________ Rep 2________ Rep 3________					Total Solvent Extractable Content, mg/g Rep 1________ Rep 2________ Rep 3________			
Compound	Amount Found, µg/g			RRT Found			RF Used for Quantification		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
106. Pentachloronitrobenzene									
107. Phenanthrene									
108. 4, 4'-Dichlorobiphenyl									
109. Anthracene									
110. Acridine									
111. Phenanthridine									
112. Carbazole									
113. 2, 4, 5-Trichlorophenoxyacetic acid									
114. Di-n-butyl phthalate									
115. 2, 4-Dinitroaniline									
116. 2, 2', 4, 4'-Tetrachlorobiphenyl									
117. Anthraquinone									
118. Fluoranthene									
119. 2, 2', 4, 4', 6, 6'-Hexachlorobiphenyl									
120. 2-Methylanthraquinone									
121. Pyrene									
122. 4, 4'-DDE									
123. 4, 4'-DDD									
124. Diethylstilbestrol									
125. 4, 4'-DDT									
126. Triphenyl phosphate									
127. Benzo(a)anthracene									
128. Methoxychlor									
129. 3, 3'-Dichlorobenzidine									
130. Chrysene									
131. Di- (2-ethylhexyl) phthalate									
132. Tri- (p-tolyl) phosphate									
133. Di (2-ethylhexyl) sebacate									
134. Benzo(k)fluoranthene									
135. Hexachlorophene									
136. Benzo(a)pyrene									
137. Dibenzocarbazole									
138. Indeno(1, 2, 3 cd)pyrene									
139. Dibenzo(a, h)anthracene									
140. Benzo(g, h, i)perylene									

Form 23

UNLISTED SEMIVOLATILE COMPOUNDS FOUND

Laboratory ID __________

Sample ID __________

Tentative Identification	Amount Found, µg/g			RRT Found Relative to D_{10}-Phenanthrene			Characteristic Ions (Relative Intensity)			
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Ion (RI)	Ion (RI)	Ion (RI)	Ion (RI)

Form 25

RELATIVE ABUNDANCES OF DFTPP IONS IN SEMIVOLATILE COMPOUND ANALYSES

aboratory ID ________

	Relative Abundance of Given Ion												
R..	51	68	69	70	127	197	198	199	275	365	441	442	443
Avg.													
% RSD													

Form 48

RETENTION TIMES OF SEMIVOLATILE INTERNAL STANDARDS

Laboratory ID __________

	Retention Time of Given Internal Standard, seconds												
Run No.	BB	Anil	Phel	NB	Naph	Biph	Acen	DNP	Phen	DFTPP	Pyr	Chry	BaP
Avg.													
% RSD													

.B = D_5-Bromobenzene
nil = D_5-Aniline
hel = D_5-Phenol
.B = D_5-Nitrobenzene
aph = D_8-Naphthalene

Biph = D_{10}-Biphenyl
Acen = D_{10}-Acenaphthene
DNP = D_3-2,4-Dinitrophenol
Phen = D_{10}-Phenanthrene
DFTPP = Decafluorotriphenylphosphine

Pyr = D_{10}-Pyrene
Chry = D_{12}-Chrysene
BaP = D_{12}-Benzo(a)pyrene

Form 58

RESPONSE FACTORS OF SEMIVOLATILE INTERNAL STANDARDS

aboratory ID ____________

Run No.	Response Factor of Given Internal Standard Relative to D_{10}-Phenanthrene												
	BB	Anil	Phol	NB	Naph	Biph	Acen	Phen	DNP	DFTPP	Pyr	Chry	BaP
Avg.													
% RSD													

B = D_5-Bromobenzene
nil = D_5-Aniline
ol = D_5-Phenol
B = D_5-Nitrobenzene
ph = D_8-Naphthalene

Biph = D_{10}-Biphenyl
Acen = D_{10}-Acenaphthene
Phen = D_{10}- Phenanthrene
DNP = D_3-2,4-Dinitrophenol
DFTPP = Decafluorotriphenylphosphine

Pyr = D_{10}-Pyrene
Chry = D_{12}-Chrysene
BaP = D_{12}-Benzo(a)pyrene

Form 6S

SEMIVOLATILE SURROGATE STANDARD DATA

Laboratory ID ____________

Run No.	Int. Std. Level, µg/g	Conc. of Surrogate Added, µg/g	RRT of Given Surrogate			RF Used for Given Surrogate			% Recovery for Given Surrogate		
			DFB	FA	PFP	DFB	FA	PFP	DFB	FA	PFP
Avg.											
% RSD											

Compound Code: DFB = Decafluorobiphenyl FA = 2-Fluoroaniline PFP = Pentafluorophenol

Form 75

RELATIVE RETENTION TIMES OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID ____________

Compound	Relative Retention Times Obtained From GC-MS Calibration Run of Given Run Number																			Avg.	% RSD
1. 4-MePyridine																					
2. 1, 4-DClButane																					
3. Anisole																					
4. BrBenzene																					
5. 2, 4-DMePyrid																					
6. 4-ClToluene																					
7. Benzaldehyde																					
8. Thiophenol																					
9. PentaClEthane																					
10. Aniline																					
11. Phenol																					
12. BClEtEther																					
13. 2-ClPhenol																					
14. 1, 2, 4-TMeBenz																					
15. TriMePyridine																					
16. 1, 4-DClBenz																					
17. Benzyl Chlor																					
18. Benzyl Alc																					
19. 1, 2-DClBenz																					
20. 2-MePhenol																					
21. N-MeAniline																					
22. Acetophenone																					
23. 4-MePhenol																					
24. 4-MeAniline																					
25. HexClEthane																					
26. Nitrobenzene																					
27. N, N-DMeAnil																					
28. 4-t-BuPyrid																					
29. TetraMeBenz																					
30. 4-ClBenzalde																					
31. 2-NPhenol																					
32. Benzal Chlor																					
33. 2, 4-DMePhol																					
34. 2-NToluene																					
35. Tetralin																					
36. Propiophenon																					
37. 2, 6-DMeAnil																					

Form 85

RELATIVE RETENTION TIMES OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID ____________

Compound	Relative Retention Times Obtained From GC-MS Calibration Run of Given Run Number																			Avg.	% RSD
38. Benzoic Acid																					
39. 2, 6-DClPhol																					
40. 1, 2, 4-TClBenz																					
41. Naphthalene																					
42. 4-ClPhenol																					
43. 4-ClAniline																					
44. 2, 4-DClPhol																					
45. HexClPropene																					
46. 4-NToluene																					
47. HexClButadien																					
48. Benzotrichlor																					
49. 1-Cl-4-NBenz																					
50. Quinoline																					
51. BClEthoxyEth																					
52. 4-Cl-3MePhol																					
53. 4-t-BuPhenol																					
54. 2-MeNaph																					
55. 4-BrAniline																					
56. 4-Cl-2MeAnil																					
57. 4-ClBz Acid																					
58. TetraClBenz																					
59. 2, 4, 6-TClPhol																					
60. 2, 4, 5-TClPhol																					
61. Acetanilide																					
62. 2-ClNaph																					
63. Biphenyl																					
64. 1-ClNaph																					
65. 4-MeQuinoline																					
66. 2-EtNaph																					
67. Phenyl Ether																					
68. 2-NAniline																					
69. 4-BrBz Acid																					
70. 3, 4-DClAnil																					
71. 2-Cl-4-NPhol																					
72. Acenaphthylen																					
73. 2, 3-DMeNaph																					
74. 1, 3-DNBenzene																					

Form 8:

RELATIVE RETENTION TIMES OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID __________

Compound	Relative Retention Times Obtained From GC-MS Calibration Run of Given Run Number																			Avg.	% RSD
75. DiMePhthalate																					
76. 2, 6-DNToluene																					
77. 3-NAniline																					
78. Acenaphthene																					
79. 2, 4-DBuPhenol																					
80. 2, 4-DNPhenol																					
81. 2-Naphthol																					
82. 2, 6-DBuMePhol																					
83. Dibenzofuran																					
84. 4-NPhenol																					
85. PentaClBenz																					
86. 2, 4-DNToluene																					
87. 1-AminoNaph																					
88. 2, 4, 5-TClAnil																					
89. 2, 4-DNClBenz																					
90. Fluorene																					
91. 4-ClPhPhEther																					
92. 4-Cl-2NAnilin																					
93. 4-NAniline																					
94. 2-Me-4, 6-DNP																					
95. Diphenylamine																					
96. Azobenzene																					
97. Trifluralin																					
98. 2-Cl-4NAnilin																					
99. 4-HydroxyBiph																					
100. HexaClBenzene																					
101. 2, 6-DCNAnil																					
102. 2, 4-D																					
103. 4-AminoBiph																					
104. PentaClPhenol																					
105. 3, 3'-DC1Biph																					
106. PentaClNBenz																					
107. Phenanthrene																					
108. 4, 4'-DC1Biph																					
109. Anthracene																					
110. Acridine																					
111. Phenanthridine																					

Form 83

RELATIVE RETENTION TIMES OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID ____________

Compound	Relative Retention Times Obtained From GC-MS Calibration Run of Given Run Number																			Avg.	% RSD
112. Carbazole																					
113. 2, 4, 5-T																					
114. DBuPhthalate																					
115. 2, 4-DNAniline																					
116. TetraClBiph																					
117. Anthraquinone																					
118. Fluoranthene																					
119. HexaClBiph																					
120. 2-MeAnthraqu																					
121. Pyrene																					
122. DDE																					
123. DDD																					
124. DEtStilbestrol																					
125. DDT																					
126. TPhPhosphate																					
127. Bz(a)Anthr																					
128. Methoxychlor																					
129. 3, 3'-DCBzdin																					
130. Chrysene																					
131. DEtHxPhth																					
132. TTolPhosphat																					
133. DEtHxSebacate																					
134. Bz(k)Fluor																					
135. Hexachlorophe																					
136. Bz(a)Pyrene																					
137. DBzCarbazole																					
138. Indenopyrene																					
139. DBzAnthracene																					
140. Benzoperylene																					
S1. 2-F Aniline																					
S2. Penta F Phenol																					
S3. Deca F Biphen																					

Form 8S

RESPONSE FACTORS OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID____________

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																		Avg.	% RSD
1. 4-MePyridine																				
2. 1, 4-DClButane																				
3. Anisole																				
4. BrBenzene																				
5. 2, 4-DMePyrid																				
6. 4-ClToluene																				
7. Benzaldehyde																				
8. Thiophenol																				
9. PentaClEthane																				
10. Aniline																				
11. Phenol																				
12. BClEtEther																				
13. 2-ClPhenol																				
14. 1, 2, 4-TMeBenz																				
15. TriMePyridine																				
16. 1, 4-DClBenz																				
17. Benzyl Chlor																				
18. Benzyl Alc																				
19. 1, 2-DClBenz																				
20. 2-MePhenol																				
21. N-MeAniline																				
22. Acetophenone																				
23. 4-MePhenol																				
24. 4-MeAniline																				
25. HexClEthane																				
26. Nitrobenzene																				
27. N, N-DMeAnil																				
28. 4-t-BuPyrid																				
29. TetraMeBenz																				
30. 4-ClBenzalde																				
31. 2-NPhenol																				
32. Benzal Chlor																				
33. 2, 4-DMePhol																				
34. 2-NToluene																				
35. Tetralin																				
36. Propiophenon																				
37. 2, 6-DMeAnil																				

Form 98

RESPONSE FACTORS OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID__________

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																		Avg.	% RSD
38. Benzoic Acid																				
39. 2, 6-DClPhol																				
40. 1, 2, 4-TClBenz																				
41. Naphthalene																				
42. 4-ClPhenol																				
43. 4-ClAniline																				
44. 2, 4-DClPhol																				
45. HexClPropene																				
46. 4-NToluene																				
47. HexClButadien																				
48. Benzotrichlor																				
49. 1-Cl-4-NBenz																				
50. Quinoline																				
51. BClEthoxyEth																				
52. 4-Cl-3MePhol																				
53. 4-t-BuPhenol																				
54. 2-MeNaph																				
55. 4-BrAniline																				
56. 4-Cl-2MeAnil																				
57. 4-ClBz Acid																				
58. TetraClBenz																				
59. 2, 4, 6-TClPhol																				
60. 2, 4, 5-TClPhol																				
61. Acetanilide																				
62. 2-ClNaph																				
63. Biphenyl																				
64. 1-ClNaph																				
65. 4-MeQuinoline																				
66. 3-EtNaph																				
67. Phenyl Ether																				
68. 2-NAniline																				
69. 4-BrBz Acid																				
70. 3, 4-DClAnil																				
71. 2-Cl-4-NPhol																				
72. Acenaphthylen																				
73. 2, 3-DMeNaph																				
74. 1, 3-DNBenzene																				

Form 86

RESPONSE FACTORS OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID__________

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																		Avg.	% RSD
75. DiMePhthalate																				
76. 2, 6-DNToluene																				
77. 3-NAniline																				
78. Acenaphthene																				
79. 2, 4-DBuPhenol																				
80. 2, 4-DNPhenol																				
81. 2-Naphthol																				
82. 2, 6-DBuMePhol																				
83. Dibenzofuran																				
84. 4-NPhenol																				
85. PentaClBenz																				
86. 2, 4-DNToluene																				
87. 1-AminoNaph																				
88. 2, 4, 5-TClAnil																				
89. 2, 4-DNClBenz																				
90. Fluorene																				
91. 4-ClPhPhEther																				
92. 4-Cl-2NAnilin																				
93. 4-NAniline																				
94. 2-Me-4, 6-DNP																				
95. Diphenylamine																				
96. Azobenzene																				
97. Trifluralin																				
98. 2-Cl-4NAnilin																				
99. 4-HydroxyBiph																				
100. HexaClBenzene																				
101. 2, 6-DClNAnil																				
102. 2, 4-D																				
103. 4-AminoBiph																				
104. PentaClPhenol																				
105. 3, 3'-DClBiph																				
106. PentaClNBenz																				
107. Phenanthrene																				
108. 4, 4'-DClBiph																				
109. Anthracene																				
110. Acridine																				
111. Phenanthridine																				

Form 98

RESPONSE FACTORS OF SEMIVOLATILE COMPOUNDS FROM CALIBRATION RUNS

Laboratory ID __________

Compound	Response Factors Obtained From GC-MS Calibration Run of Given Run Number																		Avg.	% RSD
112. Carbazole																				
113. 2, 4, 5-T																				
114. DBuPhthalate																				
115. 2, 4-DNAniline																				
116. TetraClBiph																				
117. Anthraquinone																				
118. Fluoranthene																				
119. HexaClBiph																				
120. 2-MeAnthraqu																				
121. Pyrene																				
122. DDE																				
123. DDD																				
124. DEtStilbestrol																				
125. DDT																				
126. TPhPhosphate																				
127. Bz(a)Anthr																				
128. Methoxychlor																				
129. 3, 3'-DCBzdin																				
130. Chrysene																				
131. DEtHxPhth																				
132. TTolPhosphat																				
133. DEtHxSebacate																				
134. Bz(k)Fluor																				
135. Hexachloropho																				
136. Bz(a)Pyrene																				
137. DBzCarbazole																				
138. Indenopyrene																				
139. DBzAnthracene																				
140. Benzoperylene																				
S1. 2-F Aniline																				
S2. Penta F Phenol																				
S3. Deca F Biphen																				

Form 96